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MAMMALIAN TOXICOLOGICAL EVALUATION OF TNT WASTEWATERS

Volume I
Chemistry Studies

By

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The objectives of this study were to identify the chemical components of two types of wastewaters discharged from Army munitions facilities and to supply quantitative data on each component. These data were used to establish representative ratios of the chemical components in the discharges. Data were obtained over 12-month sampling period to establish TNT/RDX ratios from Iowa and Milan Army Ammunition Plants and the relative percentages of more than 30 components in the condensate discharge at Volunteer Army Ammunition Plant.

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1,5-dimethyl-2,4-dinitrobenzene; 2,3-dinitrotoluene; [illegible]-dinitrotoluene; 4-amino-3,5-dinitrotoluene; toluene; 4-nitrotoluene; 2,4-din[illegible]-5-methylphenol; 2-amino-6-nitrotoluene; 3-amino-4-nitrotoluene; 2-nitrotoluene; 2,3,6-trinitrotoluene; 2-amino-4,6-dinitrotoluene; 5-methyl-2-nitrophenol; 2-amino-4-nitrotoluene; 3-methyl-2-nitrophenol; 1,3,5-trinitrobenzene; 3,5-dinitroaniline; 3-nitrobenzonitrile; 4-nitrobenzonitrile; 2-amino-3,6-dinitrotoluene; photoirradiation, synthesis, analytical characterization, environmental fate

20. ABSTRACT (Continued)

Analytical methods were developed to study the effects of sunlight on the discharges, and methods were developed to prepare photoirradiated residues under laboratory conditions for toxicity testing.

Synthetic methods were developed to procure those wastewater components that were not commercially available, and analytical characterizations of all chemicals used in toxicity testing were obtained.

Finally, preliminary estimates of the roles of volatility and photolysis in describing the environmental fate of condensate components in aqueous discharges were established.

EXECUTIVE SUMMARY

The objective of this research was to generate a data base for munitions-unique pollutants being discharged at load, assemble, and pack (LAP) facilities and for condensate discharges at a 2,4,6-trinitrotoluene (TNT) production facility. These data were used to establish environmentally realistic wastewater discharge mixtures for use in toxicological testing in aquatic and mammalian species.

The major components of LAP discharges evaluated were TNT and 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX). A TNT/RDX ratio of 1.6/1.0 was established for wastewaters discharged from shell washout and housecleaning operations. Since extensive photochemical degradation of TNT occurs in sunlight, laboratory methods were developed to simulate sunlight in generating photoirradiated TNT/RDX residues for the toxicological evaluations.

In the condensate discharge, the following compounds were identified and quantified over a 12-month sampling period: N-nitrosomorpholine; N-morpholinoacetonitrile; 2,4-dinitrotoluene; 2,6-dinitrotoluene; 1,3-dinitrobenzene; 3-amino-2,4-dinitrotoluene; 3-amino-2,6-dinitrotoluene; 5-amino-2,4-dinitrotoluene; 3,5-dinitrotoluene; 3,4-dinitrotoluene; 4-amino-2,6-dinitrotoluene; 1,5-dimethyl-2,4-dinitrobenzene; 2,3-dinitrotoluene; 2,5-dinitrotoluene; 4-amino-3,5-dinitrotoluene; toluene; 4-nitrotoluene; 2,4-dinitro-5-methylphenol; 2-amino-6-nitrotoluene; 3-amino-4-nitrotoluene; 2-nitrotoluene; 2,3,6-trinitrotoluene; 2-amino-4,6-dinitrotoluene; 5-methyl-2-nitrophenol; 2-amino-4-nitrotoluene; 3-methyl-2-nitrophenol; 1,3,5-trinitrobenzene; 3,5-dinitroaniline; 3-nitrobenzonitrile; 4-nitrobenzonitrile; 2-amino-3,6-dinitrotoluene; and 2,4,6-trinitrotoluene. Through cluster analysis and 90th percentile concentration determinations, a representative discharge distribution of condensate components was established.

Methods were developed for the synthesis of those condensate components that could not be obtained from commercial sources. All condensate components that were to be used in the toxicological evaluations were identified and analyzed for purity through analytical characterizations using spectrometric and chromatographic techniques.

Hypotheses about the environmental fates of condensate components were examined. Volatilization and photolysis appear to play major roles in the transport and transformation of these compounds in the aquatic environment.

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1 INTRODUCTION

The U.S. Army Medical Research and Development Command has been directed to evaluate the potential hazard to mammalian and aquatic systems of wastewater discharged from TNT production and handling facilities. Of primary concern is the potential toxicity of the complex mixture that results from the photodegradation of TNT and RDX, a mixture commonly referred to as LAP (load, assemble, and pack) wastewater. Also of concern are the wastewaters generated at TNT production facilities known as condensate water.

Under contract with USAMRDC, SRI International undertook extensive chemical and toxicological studies, the respective objectives of which were to identify and quantify the chemical components of LAP water and the photolytic changes they may undergo and to evaluate the toxicity of TNT and those TNT-containing mixtures. The goal was to determine the responses of mammals and aquatic organisms to long-term exposure to the compounds found in the wastewater discharges. This information will aid the Army to develop a data base for recommending ambient water quality criteria and for defining levels of treatment in its pollution abatement programs.

This report summarizes SRI's chemistry studies during the period 1 April 1976 to 1 March 1978. Experiments were conducted to identify and quantify chemical components in LAP water and in condensate water effluents from Army munitions plants, and these components were prepared in sufficient quantities for the toxicological evaluations. The chemical components prepared included photoirradiated and nonphotoirradiated TNT/RDX mixtures (synthetic LAP water) and a synthetic condensate mixture formulated from numerous samplings of TNT production wastewater. The results of the analytical chemistry evaluation of the condensate components used in toxicological evaluations are presented.

This report also assesses the roles of volatility and photolysis in describing the environmental fate of condensate components.

2 BACKGROUND AND OBJECTIVES

In the production of munitions compounds, significant amounts of wastewaters are generated and eventually discharged into the environment. These discharges contain many organic chemicals for which toxicological data are sparse or for which environmental fates are not known.

Before ambient water quality criteria for these discharges can be established, the chemicals in the discharge must be identified and toxicological data must be obtained for each. However, when many chemical components are discharged, the toxicological data often may be influenced by synergistic or antagonistic effects arising from interactions between the components. This can lead to incorrect assessments of toxicological hazard.

A solution to this problem is to conduct toxicologic evaluations of representative mixtures of the chemical components in the discharges. This approach is more realistic for assessing the environmental impact of the discharge and is significantly less costly than testing single compounds if long-term toxicological testing is warranted.

The objectives of the analytical chemistry segment of this study were: (1) to establish TNT/RDX ratios representative of discharges at LAP facilities; (2) to investigate laboratory methods to prepare photoirradiated residues for toxicological evaluation; (3) to identify and establish representative distributions of organics in condensate discharges at a TNT production facility; (4) to procure, via synthetic routes or commercial sources, the organic compounds identified; and (5) to supply analytically characterized samples and mixtures for toxicological evaluation. After these objectives were met, the factors affecting the environmental fate of condensate compounds in aquatic systems were investigated.

3 EXPERIMENTAL APPROACH

3.1 Sources and Analysis of LAP Wastewater Samples

3.1.1 Sources

The LAP wastewater samples investigated in this study were obtained from Iowa Army Ammunition Plant (IAAP; Burlington, Iowa) and from Milan Army Ammunition Plant (MAAP; Milan, Tennessee). Several samples of LAP discharges also investigated were from Louisiana Army Ammunition Plant (LAAP; Minden, Louisiana) and from Lone Star Army Ammunition Plant (LSAAP; Texarkana, Texas).

The LAP discharges were obtained from the Composition (Comp) B lines at IAAP and MAAP. Comp B is a mixture of TNT (60%) and RDX (40%). These discharges may undergo photolytic decomposition to create what is called "pink water." The principal chemical investigations were to establish representative ratios of TNT and RDX in numerous samples taken over a 12-month period and to develop photolytic methods to generate pink water. Both nonirradiated and irradiated LAP water were submitted for toxicological evaluation.

The majority of wastewater samples were obtained on site by U.S. Army Medical Bioengineering Research and Development Laboratory or SRI personnel and hand carried or mailed to SRI laboratories for analysis. In a few cases, sampling was performed by plant personnel and samples were mailed to SRI.

3.1.2 Analytical Methods

The determination of TNT and RDX in munitions wastewaters was performed by high-pressure liquid chromatography (hplc) using reverse-phase methods. The conditions for these analyses were--

- Instrument: Spectra-Physics Model 3500 B Liquid Chromatograph.
- Column: 30 cm x 1 cm C_{18}-μ Bondapak Reverse-Phase (Water's Assoc.).
- Solvent: Methanol/water, 60/40.
- Flow rate: 1.6 ml/min.
- Detection: uv at 254 nm.
- Sensitivity: 0.0025 aufs (absorbance units full scale).
- Retention time: 149 sec RDX; 209 sec TNT; 351 sec benzophenone (internal standard).

The lower limits of detection were 0.4 ppm for RDX and 0.1 ppm for TNT at 254 nm. These limits could be lowered by a factor of 2 at 210 nm. The latter wavelengths were used for very low TNT and RDX concentrations.

Peak areas were determined by digital integration using a Spectra-Physics Minigrator. Quantitation was achieved by the internal standard method using benzophenone as the internal standard.

Samples were received by mail in Teflon-lined, screw-cap glass bottles. They were stored under refrigeration until the time of analysis. The sample bottles were heated on a steam bath (100° C), filtered through sintered glass funnel, and analyzed by hplc. Many of the samples were also analyzed for nitrite by a modified Griess reagent[1] and for nitrate by cadmium column reduction[2] or by an ion-specific electrode. Other parameters that were monitored were pH, determined with an Orion Model 701 digital pH meter, and total organic carbon, determined with a Beckman Model 915A TOC analyzer.

3.1.3 Sampling Data

Iowa Army Ammunition Plant

At IAAP, pollution abatement is practiced by passing shell washout and housecleaning wastewaters through diatomaceous earth filters and carbon columns before discharge. Wastewater samples were collected at points before the carbon column (influent) and immediately after the carbon column (effluent). Tables 1 and 2 present the analytical results for the influent samples and the effluent samples, respectively. In some cases, the aqueous solubility of TNT and RDX were exceeded. In these cases, hot aliquots from the sample bottles were diluted prior to analysis.

In the influent samples, the TNT concentration ranged from 50.0 to 259 mg/liter, with a mean of 161.3 mg/liter. RDX concentrations ranged from 23.8 to 173 mg/liter, with a mean value of 80.5 mg/liter. The TNT/RDX ratio ranged from 1.27 to 3.82, with a mean value of 2.26.

In the effluent samples, the TNT concentration ranged from less than 0.05 to 24.3 mg/liter, with a mean value of 1.32 mg/liter. RDX concentrations ranged from less than 0.1 to 24.2 mg/liter, with a mean of 1.53 mg/liter. The TNT/RDX ratios for effluents were derived from samples that had non-zero denominators. The mathematically definable ratios ranged from 0 to 2.00 and had a mean value of 0.5[illegible]

Milan Army Ammunition Plant

At MAAP, munition-containing wastewater is directed to sumps where the insolubles settle, and it overflows into a small stream leaving the plant area. Samples were taken at the sumps of Area D and at a small bridge crossing the road entrance to Area D. Table 3 presents the sampling data.

From 30 samples, the TNT concentrations ranged from less than 0.05 to 210 mg/liter, with a mean value of 20.0 mg/liter. In those samples, RDX concentrations ranged from 0.1 to 109 mg/liter, with a mean value of 11.9 mg/liter. The TNT/RDX ratios varied from 0 to 2.88, with a mean value of 1.02 for sump effluents.

Table 1

COMBINED INFLUENT DATA FOR IAAP

(Milligrams per Liter)

Date (1976)	Description	TNT	RDX	TNT/RDX	NO_2^-	NO_3^-	pH	TOC
2/23	Precolumn, Line 2	117	*	--	--	--	7.92	--
2/23	Precolumn, Line 3A	87	36	2.42	--	--	7.85	--
2/23	Precolumn, Line 1	52	*	--	--	--	8.11	--
3/29	Precolumn, Line 3A	119	39.6	3.01	--	--	7.62	--
4/27	Precolumn, Line 3A	129	41	3.14	5.1	3.3	7.27	--
5/24	Precolumn, Line 3A	219	98.3	2.22	5.8	2.6	7.26	--
6/24	Precolumn, Line 3A	184	62	2.99	0.6	14.9	7.58	--
8/5	Precolumn, Line 3A	150	62.7	2.39	0.8	25.8	8.53	78
8/9	Precolumn, Line 3A	91	23.8	3.82	1.2	31.5	7.82	63
8/9	Precolumn, Line 3A	190	50	3.80	2.9	48.6	8.11	103
8/16	Precolumn, Line 3A	208	95.4	2.18	0.87	26.0	7.73	107
8/16	Precolumn, Line 3A	206	133	1.55	2.0	27.1	7.68	107
8/19	Precolumn, Line 3A	230	149	1.54	0.87	36	7.79	138
8/18	Precolumn, Line 3A	124	55.1	2.25	0.57	26.1	7.93	60
8/20	Precolumn, Line 3A	50	35.1	1.42	0.29	34	8.00	37.5
8/23	Precolumn, Line 3A	103	60.8	1.69	0.95	39	7.83	67.5
8/25	Precolumn, Line 3A	245	112	2.19	0.89	31	7.80	116
8/27	Precolumn, Line 3A	259	139	1.86	2.3	16	7.15	99
8/30	Precolumn, Line 3A	220	173	1.27	1.9	17.5	7.60	106
9/1	Precolumn, Line 3A	217	154	1.41	2.2	16.0	8.15	106
8/27	Precolumn, Line 3A	208	89	2.34	2.0	35.5	7.98	106
8/27	Holding Tank	203	81	2.51	2.0	24.0	8.04	108
9/3	Line 31, Column 21	55.4	30.9	1.79	0.23	10.0	[illegible]	43
9/7	Line 31, Column 21	123	87.6	1.40	0.55	[illegible]	[illegible]	87.6

* Less than 0.1 mg/liter.

--Not determined.

Table 2

COMBINED EFFLUENT DATA FOR IAAP

(Milligrams per Liter)

Date (1976)	Description	TNT	RDX	TNT/RDX	NO_2-	NO_3-	pH	TOC
2/26	Carbon column, Line 2-14	10	*	--	--	--	8.36	--
2/26	Carbon column, Line 3A-19	24.3	24.2	1.00	--	--	7.55	--
2/26	Carbon column, Line 1-5	**	*	--	--	--	7.85	--
3/29	Carbon column	0.1	*	--	--	--	7.40	--
4/26	Carbon column, Line 3A	0.3	*	--	1.8	9.5	7.32	--
5/25	Carbon column, Line 3A	0.5	1.1	0.45	3.6	5.4	7.36	--
6/25	Carbon column, Line 3A	0.3	*	--	9.2	3.1	7.07	--
8/5	Carbon column, Line 3A	**	*	--	2.06	23	8.87	<1
8/9	Carbon column, Line 3A	**	*	--	1.6	17.7	8.36	<1
8/9	Carbon column, Line 3A	**	*	--	2.0	25	8.54	<1
8/12	Carbon column, Line 3A	0.85	*	--	2.3	22.2	8.05	4
8/16	Carbon column, Line 3A	0.23	1.1	0.21	1.4	25.5	7.64	4
8/16	Carbon column, Line 3A	0.93	1.3	0.71	1.1	24.2	7.31	4.5
8/19	Carbon column, Line 3A	0.3	2.2	0.14	0.89	22.0	7.80	2
8/18	Carbon column, Line 3A	0.15	0.9	0.17	0.92	5.4	8.12	<1
8/20	Carbon column, Line 3A	0.3	0.6	0.50	<0.01	10.0	7.68	3
8/23	Carbon column, Line 3A	**	0.5	--	2.8	9.0	7.96	7.5
8/25	Carbon column, Line 3A	**	*	--	1.7	19.0	7.97	8.0
8/27	Carbon column, Line 3A	0.45	*	--	2.5	8.4	7.48	9
8/30	Carbon column, Line 3A	**	1.6	--	3.4	10.7	7.93	7
9/1	Carbon column, Line 3A	0.15	*	--	4.1	20	8.22	9
9/7	Carbon column, Line 3A	**	*	--	1.7	4.0	8.00	7
9/3	Carbon column, Line 3A	6.2	0.1	2.00	0.25	6.0	8.11	4

*Less than 0.1 mg/liter.
**Less than 0.05 mg/liter.
--Not determined.

Table 3

COMBINED SAMPLING DATA FOR MAAP

(Milligrams per Liter)

Date (1976)	Location/ Description	TNT	RDX	TNT/ RDX	NO_2^-	NO_3^-	pH	TOC
2/25	Presump, Line D41	80.5	28	2.88	--	--	6.39	--
2/25	After sump, Line D41	70.6	38	1.86	--	--	6.52	--
2/25	Plant D discharge	27.4	19	1.44	--	--	7.02	--
2/25	Plant X discharge	1.1	5	0.22	--	--	6.75	--
4/26	Plant X discharge	0.1	*	--	0.1	4.2	5.82	--
4/26	Plant D discharge	0.7	2.0	0.35	0.7	5.2	5.00	--
6/24	Plant X Bldg. 41	25.5	15.4	1.66	0.05	8.8	6.31	--
6/24	Plant D, sump	2.4	3.2	0.75	0.05	13.3	6.13	--
7/26	X-41-Cleaning	210	109	1.93	0.2	130	6.90	122
7/26	X-41-Comp B	1.7	1.3	1.31	**	5.7	6.19	< 1
7/26	X-41-Washings	117	48.2	2.43	**	680	6.25	71
7/26	X-41-Kettle cleanup	5.6	9.6	6.58	**	4.6	6.95	1
7/28	X-41-Comp B	***	1.4	--	**	6.1	6.40	< 1
7/30	X-41-Comp B 0900	6.3	3.6	1.75	**	6.8	5.90	3
7/30	X-41-Comp B 1000	4.1	5.2	0.79	**	6.2	6.12	1
7/30	X-41-Comp B 1100	***	0.5	--	0.04	6.4	6.17	< 1
8/2	X-41-Comp B 0900	4.6	4.7	0.98	**	7.4	6.90	3
8/2	X-41-Comp B 1000	***	1.6	--	0.06	7.0	7.28	< 1
8/5	X-41-Comp B 1000	0.8	0.7	1.14	**	6.1	6.19	< 1
8/26	Line X effluent	5.7	4.2	1.36	**	9.0	6.90	3.5
8/26	Line D effluent	2.3	5.6	0.41	**	9.4	7.53	3.0
9/13	X-41 effluent	5.3	6.1	0.87	**	4.2	6.20	4.5
9/14	X-41 effluent	5.3	3.8	1.39	**	8.2	6.87	3
9/15	X-41 effluent	6.7	8.7	0.77	**	10.2	6.51	6
9/16	X-41 effluent	6.3	7.5	0.84	**	10.0	6.03	6
9/17	X-41 effluent	6.8	5.8	1.17	**	7.9	6.52	3
8/20	X-41 effluent	4.4	[illegible]	1.29	0.02	10	7.50	7
8/23	X-41 effluent	1.6	2.6	0.62	0.04	8.6	7.31	6.5
8/24	X-41 effluent	3.8	3.7	1.03	0.06	8.6	7.41	6.5
8/25	X-41 effluent	5.4	4.1	1.32	**	9.6	7.26	4.5

*Less than 0.1 mg/liter.

**Less than 0.02 mg/liter.

***Less than 0.05 mg/liter.

--Not determined.

Louisiana Army Ammunition Plant

LAAP directs its wastewaters to sumps. During the sampling period, the sump effluents wer trucked from the sumps to lagoons. Photolytic decomposition of TNT and RDX occurs in the lagoons, and the environment may become contaminated during extremely heavy rains when the lagoons overflow. Table 4 presents the data on the four samples obtained at LAAP from sump and lagoon locations.

In the samples, the mean TNT/RDX ratio was 1.83, whereas the lagoon samples had a mean ratio of 0.39. This indicates that TNT has a greater photolytic reactivity than RDX and that the TNT/RDX ratio is dynamic.

Lone Star Army Ammunition Plant

LSAAP handles its wastewaters similarly to LAAP, using sumps and lagoons. Table 5 presents the data on the several samples taken from the lagoons and from areas around the lagoons. (LSAAP was not operating during the sampling period, so these data were not included in the formulation of TNT/RDX ratios.)

3.2 Establishment of a TNT/RDX Ratio

As TNT and RDX are discharged into the environment, the ratio of the two components becomes highly dynamic, principally because of the high photochemical reactivity of TNT. Therefore, such factors as the time of day or year and intensity of sunlight influence the ratio greatly.

For initiation of the toxicological evaluations, a ratio was selected that would represent the worst condition--no pollution abatement before wastewater discharge. This condition is represented by IAAP influent, MAAP sump effluent, and LAAP sump effluent data. Averaging of these data resulted in the establishment of a

Table 4

COMBINED SAMPLING DATA FOR LAAP

(Milligrams per Liter)

Date (1976)	Location	TNT	RDX	TNT/ RDX	NO_2^-	NO_3^-	pH	TOC
2/26	Ditch runoff from Red Water Lagoon	*	**	--	--	--	7.51	--
2/26	Lagoon - red water	26	35	0.74	--	--	8.18	--
2/26	Sump - melt and pour facility	78	34	2.29	--	--	7.82	--
2/26	Road ditch near melt and pour facility	1	6	0.17	--	--	8.78	--
5/24	Active pit	30	102	0.29	25.3	7.8	7.81	--
5/24	S-Line	201	113	1.78	19.3	150	7.54	--
5/24	Healthy pit	1.1	2.8	0.39	0.5	15.4	7.85	--
6/24	Active pit	43.9	85.5	0.51	0.7	110	8.25	--
6/24	Sump Line S	275	189	1.46	12.2	221	7.94	--
8/26	Pond S - no rain	2.7	82	0.03	6.9	56	8.35	135
8/26	Line 5 sump	123	68	1.80	102	39	7.75	77

*Less than 0.05 mg/liter.
**Less than 0.1 mg/liter.
--Not determined.

Table 5

COMBINED SAMPLING DATA FOR LSAAP

(Milligrams per Liter)

Date (1976)	Location	TNT	RDX	TNT/ RDX	NO_2^-	NO_3^-	pH	TOC
2/25	Sump effluent, Area O	116	82	1.41	--	--	7.46	--
2/25	Settling pond, Area O	1.4	16	0.09	--	--	7.24	--
2/25	Surface drainage at 6th St.	*	5	--	--	--	6.78	--
2/25	Second settling pond	0.1	13	0.01	--	--	6.10	--
4/28	Settling pond, Area O	5.1	10.3	0.49	3.2	25	7.13	--
4/28	6th St. discharge	*	**	--	0.1	3.8	6.60	--

*Less than 0.05 mg/liter.
**Less than 0.1 mg/liter.
--Not determined.

representative TNT/RDX ratio. From the data points in Table 6, a mean ratio value was determined to be 1.62 with a standard deviation of 0.90. The coefficient of variation for the ratio was 0.55.

3.3 Analysis of TNT/RDX Mixtures in Feed for Toxicological Evaluation

To assure for the toxicity evaluations that animal diet preparations were mixed correctly and that TNT/RDX concentrations were administered at the correct dosing levels, analytical methods were developed to determine TNT and RDX in animal feeds. The procedure established was found to work satisfactorily.

To 10 g of feed containing TNT and RDX was added 50 ml of dichloromethane, and the suspension was stirred for 30 min with a magnetic stir-bar. The suspension was filtered through a pad of Celite, and the filtrate was passed through a 2-inch column of Florisil that had been deactivated with 5% water. (The Florisil must be deactivated with water before the complete recovery of RDX can be attained.) The column was washed with 100 ml of dichloromethane, and the extracts were rotary evaporated to dryness. The residue was taken up in ethyl acetate and quantified by reverse-phase hplc as described in Section 3.1.2. The recovery of both compounds was 99%.

For determination of the stability of TNT and RDX in feed, stock feed diets were analyzed weekly for 4 weeks. At the end of that period, a greater than 95% recovery of both TNT and RDX was achieved.

Table 6

DATA POINTS USED TO ESTABLISH A REPRESENTATIVE TNT/RDX RATIO

Date (1976)	AAP	TNT/RDX
8/5	IAAP col. infl.	2.39
8/9	IAAP col. infl.	3.82
8/12	IAAP Col. infl.	3.04
8/16	IAAP col. infl.	2.18
8/16	IAAP col. infl.	1.55
8/19	IAAP col. infl.	1.54
8/18	IAAP col. infl.	2.25
8/20	IAAP col. infl.	1.42
8/23	IAAP col. infl.	1.69
8/25	IAAP col. infl.	2.19
8/27	IAAP col. infl.	1.86
8/30	IAAP col. infl.	1.27
9/1	IAAP col. infl.	1.41
8/27	IAAP col. infl.	1.79
9/3	IAAP col. infl.	1.40
2/23	IAAP col. infl.	2.42
6/24	IAAP col. infl.	2.99
4/27	IAAP col. infl.	3.14
5/24	IAAP col. infl.	2.23
3/29	IAAP col. infl.	3.00
2/23	IAAP col. infl.	2.34
7/26	MAAP sump effl.	1.93
7/26	MAAP sump effl.	1.31
7/26	MAAP sump effl.	2.43
7/26	MAAP sump effl.	0.58
7/28	MAAP sump effl.	0
7/30	MAAP sump effl.	1.75
7/30	MAAP sump effl.	0.79
8/2	MAAP sump effl.	0.98
8/5	MAAP sump effl.	1.14
9/15	MAAP sump effl.	0.77
9/16	MAAP sump effl.	0.84
9/17	MAAP sump effl.	1.17
9/13	MAAP sump effl.	0.87
9/14	MAAP sump effl.	[illegible]
8/26	MAAP sump effl.	1.
8/26	MAAP sump effl.	0.41
6/24	MAAP sump effl.	1.66
2/25	MAAP sump effl.	1.86
8/20	MAAP sump effl.	1.29
8/23	MAAP sump effl.	0.62
8/24	MAAP sump effl.	1.03
8/25	MAAP sump effl.	1.32
2/26	LAAP sump	2.29
5/24	LAAP sump	1.78
6/24	LAAP sump	1.46
8/26	LAAP sump	1.80

mean $\bar{x}$ = 1.62; SD σ = 0.90; Coeff. Var. $\sigma/\bar{x}$ = 0.55.

3.4 Preparation of Photolyzed TNT/RDX Residues

LAP wastewater photodegrades in sunlight producing--and introducing into the environment--a complex mixture of components. Evaluation of the toxicological properties of this mixture required the development of laboratory methods that approximate sunlight conditions to produce photoirradiated residues and to assess the effects of photoirradiation as a function of time.

3.4.1 Analytical Methods and Sample Profiling

TNT and RDX concentrations were determined by reverse-phase hplc as described in Section 3.1.2. To profile the photolysis products, the photolyzed solutions were acidified to pH 1 and extracted twice with diethyl ether. The ether extracts were combined, dried over anhydrous sodium sulfate, and concentrated by rotary evaporation. The extracts were then chromatographed under the following conditions:

- Instrument: Spectra-Physics Model 3500B Liquid Chromatograph.
- Column: 1/4 inch x 30 cm μ-Porasil (Waters Assoc.).
- Solvent: (A) Hexane; (B) CH_2Cl_2/CH_3OH/isopropyl alcohol (79/15/6, by volume).
- Gradient: 5% (B) in (A) 4-min delay; program to 94% (B) in (A) in 76-min sweep time using a linear gradient program.
- Flow rate: 1.2 ml/min.
- Detector: uv at 254 nm.

To prevent the chromatographic trace from offscale deflection due to the change in solvent gradient, a duplicate column was placed parallel with the working column. The solvent line was split before the injector to run solvent to the duplicate column and through the reference cell of the detector. By this technique, baseline drift was kept to a minimum.

3.4.2 Photolytic Methods

A flow-through photolytic reactor was designed to prepare TNT/RDX photoirradiated residues for toxicological evaluation. Figure 1 is a

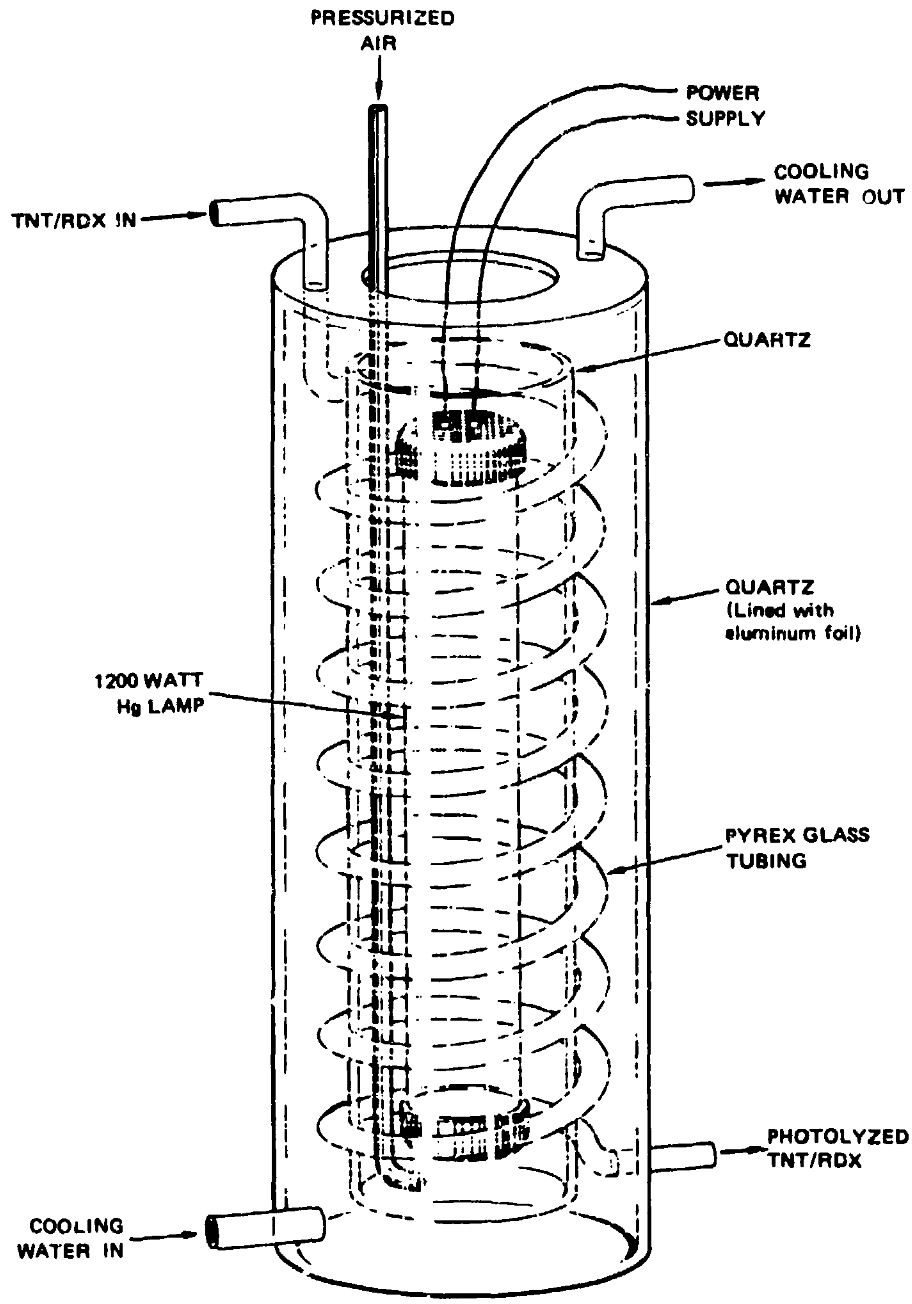


FIGURE 1 DIAGRAM OF FLOW-THROUGH PHOTOLYTIC REACTOR

diagram of the reactor system. The reactor is a quartz immersion well reactor containing a Pyrex glass coil around the lamp well. Pyrex is used to filter out wavelengths below 294 nm and pass wavelengths above 294 nm, which approximate sunlight. The light source is a Hanovia 1200-watt, medium-pressure mercury lamp operating at 310 volts. The lamp is cooled by pressurized airflow, and the reactor and Pyrex coils are cooled by tap water entering at 22° C and exiting at 28° C, at a flow rate of 6 liters/min.

TNT/RDX solutions are pumped at controlled flow rates using a Masterflex pump, and Viton tubing is used throughout because of its low absorptive properties. The solution is introduced at the top of the reactor to sweep precipitate materials from the Pyrex surfaces.

For the large-scale production of photolyzed materials, four reactors were placed in a series, and solution flow rates were increased by a factor of 4. Cooling water was introduced into each reactor individually. To conserve water, we used a 10-gallon water chiller equipped with a 1-ton condenser unit, and water was recycled via submersible pumps. This unit was suitable for cooling two reactor units, and the remaining two reactor units were cooled by tap water.

3.4.3 Laboratory and Sunlight Photolysis

For comparative studies in natural sunlight, TNT/RDX solutions were placed on a rooftop in a glass crystallizing dish (90 x 100 mm) covered on all sides so that light could enter the solution only through the surface. The solution was stirred with a magnetic stir bar. These experiments were performed on warm summer days in June and July at SRI's headquarters in Menlo Park, California.

The rooftop studies were performed to generate chromatographic profiles that could then be compared with chromatographic profiles generated by the laboratory reactor system. These rooftop studies showed that TNT photodecomposition followed zero-order kinetics and was independent of RDX. However, the rate of photodecomposition of RDX was highly dependent on the presence of TNT. Figure 2 illustrates the changes in concentration of TNT and RDX as a mixture and alone with exposure to sunlight. RDX photodegraded approximately five times faster in the absence of TNT. Possible explanations for this are that, in the TNT/RDX mixture, RDX cannot compete successfully for the light or that photolytically excited states of RDX are quenched by TNT and its photoproducts.

As shown in Figure 3, the photodegradations of TNT and RDX in the laboratory flow-through reactor depended on flow rate (residence time) and increased rapidly at low flow rates (100 to 10 ml/min). The relative degradation rates of TNT and RDX approximated those of the components alone in sunlight.

To assure that the mercury lamp photolysis was yielding a similar distribution of TNT/RDX photoproducts as sunlight, chromatographic profiles of rooftop and laboratory photolysis for similar levels of TNT photodegradation were compared using normal phase hplc (Section 3.4.1). Figure 4 presents the chromatographic profiles for the mercury lamp and sunlight photolyses at 99% TNT photodegradation. This end point was selected as a "best-case" condition based on previous toxicological data[3] that showed acute toxicity (to both mammals and fish) decreased as a function of photolysis. The profiles match closely, indicating that light from the mercury lamp filtered through Pyrex is a reasonable approximation of photolysis by sunlight for TNT/RDX mixtures. Components in the profile were tentatively identified (see Figure 4) by comparison of their retention times with those of known standards.

3.4.4 Establishment of a Photoirradiation End Point

Once the artificial light source and flow through reactor system had been developed, the next task was to determine a flow rate through the reactor that defined the TNT and RDX concentrations at a selected end point. This would yield a chemical end point that could be

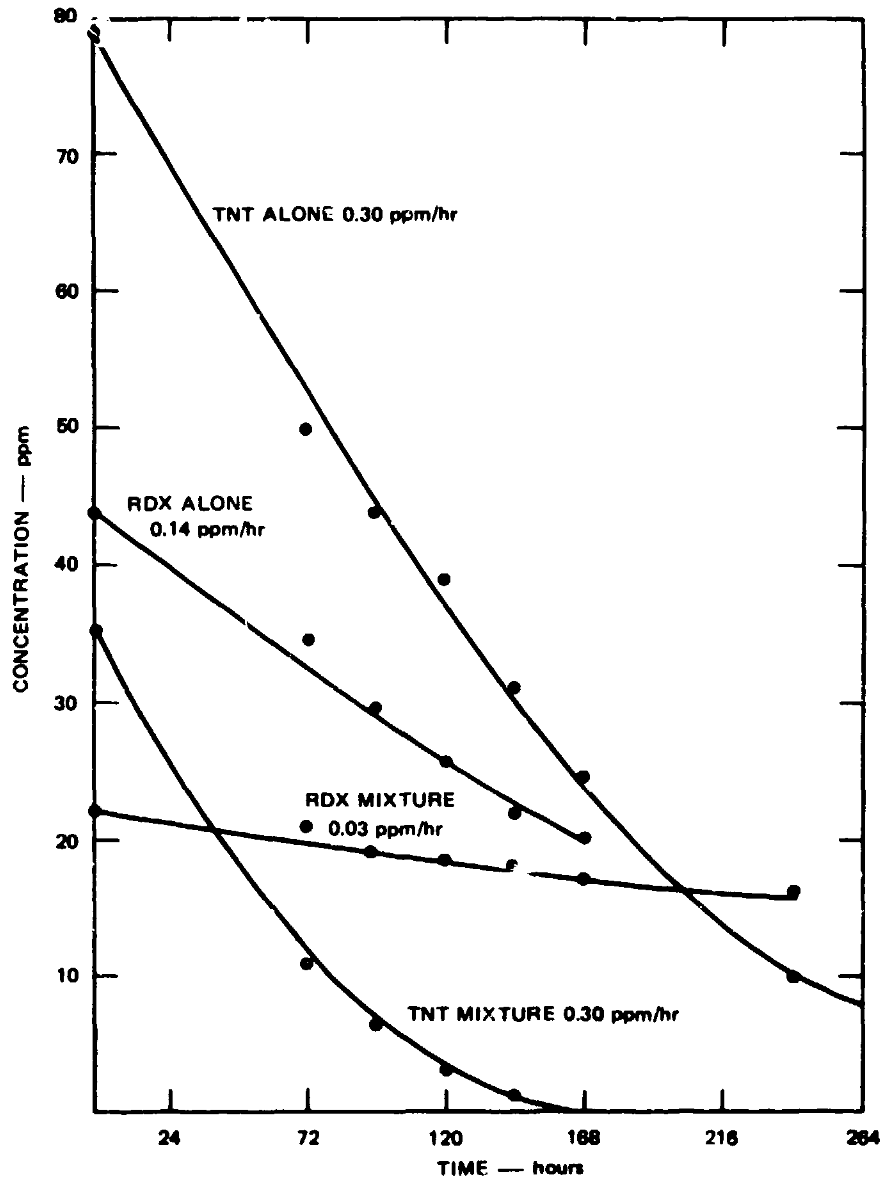


FIGURE 2 DECOMPOSITION OF TNT AND RDX (ALONE AND MIXED) IN SUNLIGHT

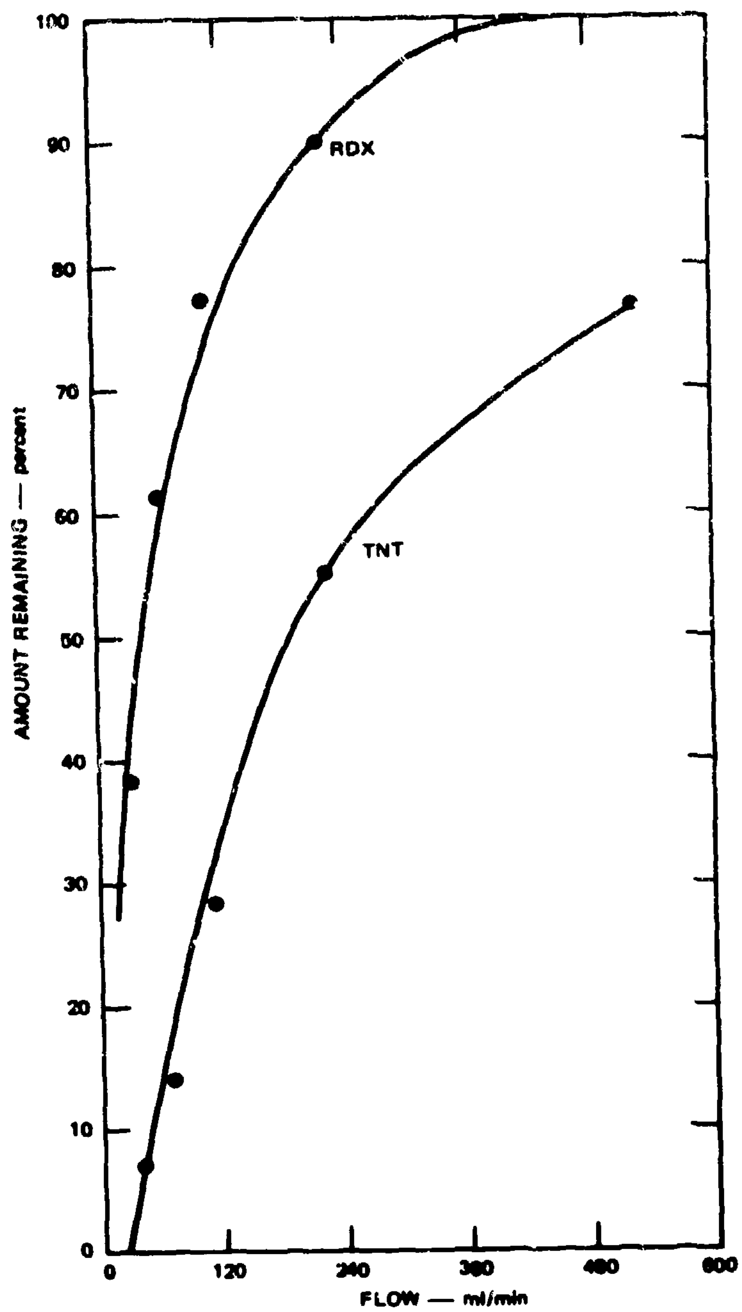


FIGURE 3 RELATIVE CONCENTRATIONS OF TNT AND RDX IN FLOW-THROUGH REACTOR AS A FUNCTION OF FLOW RATE

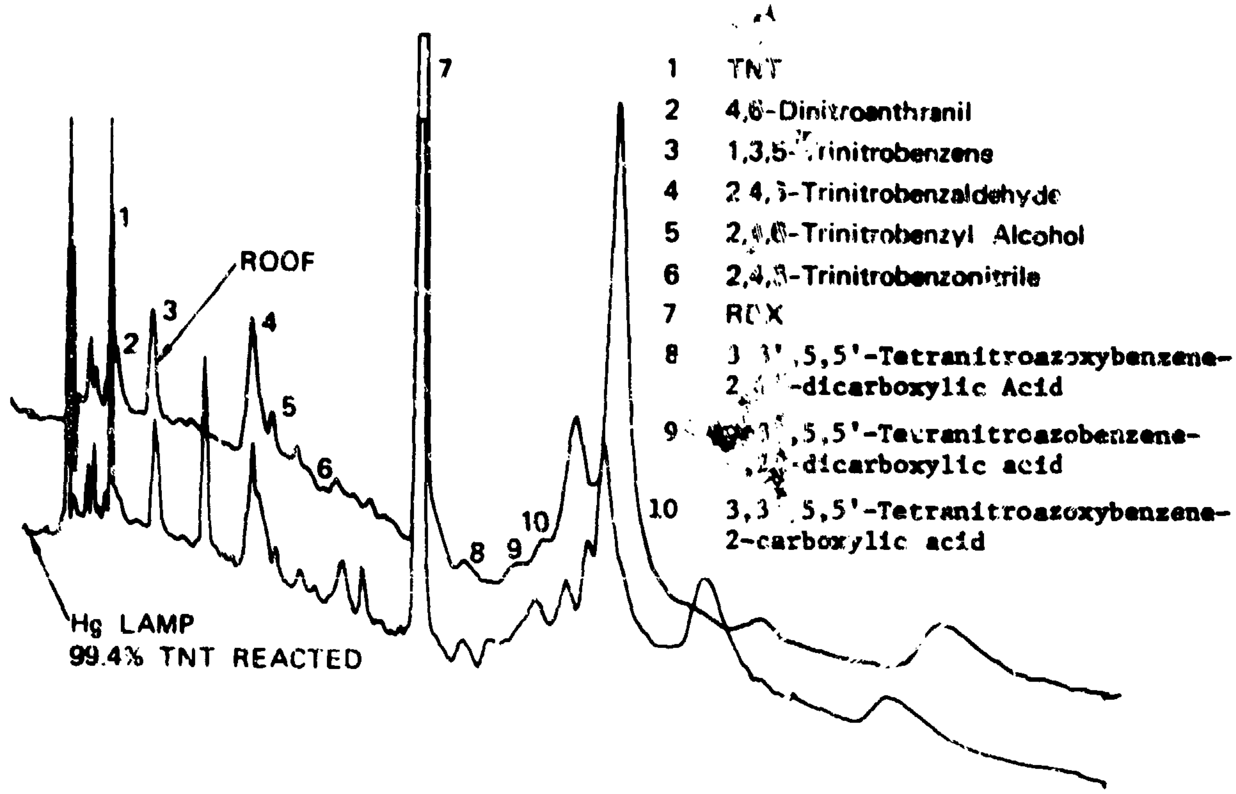


FIGURE 4 COMPARATIVE HPLC PROFILE OF THE PHOTOLYSIS OF TNT/RDX MIXTURE UNDER NATURAL SUNLIGHT (ROOF IV) AND LABORATORY (Hg LAMP) CONDITIONS

reproduced should any variations in flow rate or in light intensity in the reactor lamp occur.

The selection of the end point was based on the response of the water flea (*Daphnia magna*) to flow rate through the reactor (photolytic degradation) in "flow-versus-toxicity" studies.[a] An end point was defined as the flow rate at which a stable toxicological response was obtained. Table 7 lists the TNT and RDX concentrations for different flow rates and the 48-hour EC50 values for *Daphnia magna* at each flow rate. From these data, photoirradiation end points were selected to be at TNT concentration levels of 0.1 mg/liter (± 100%) and at RDX concentrations of 2.3 mg/liter (± 100%).

Table 7

ACUTE TOXICITY TO *DAPHNIA MAGNA* OF SYNTHETIC LAP WASTEWATER PHOTOIRRADIATED AT DIFFERENT FLOW RATES

Flow (ml/min)	TNT (mg/liter)	RDX (mg/liter)	EC50 (mg/liter)
99	1.27	12.9	15.0
73	0.45	10.5	22.6
53	0[illegible]	9.3	27.1
34	[illegible]	6.5	>28.2
18	[illegible]	2.3	>28.2
10	0.[illegible]	0.07	>28.2
5.4	0.01	0.003	>28.2
0	32.0	20.2	--

3.4.5 Preparation of Photoirradiated Materials for Toxicological Evaluations

With the chemical end point defined, the following procedure was used to prepare photoirradiated materials for the mammalian toxicological evaluations:

Solutions of TNT and RDX were prepared individually in 55-gallon drums with polyethylene liners, and their respective concentrations were monitored by hplc. Then the solutions were combined to give a TNT/RDX ratio of 1.6/1.0 in another 55-gallon drum. TNT concentrations averaged 32 ppm, and RDX concentrations averaged 20 ppm. The combined solution was pumped through the four-unit photolytic reactor system at 60 to 100 ml/min. The photolysate was collected in a 55-gallon drum and acidified to pH 1.5; 3-liter portions were extracted with 1-liter portions of diethyl ether. The ether extracts were combined and rotary evaporated for removal of the majority of the ether. The remaining extract was frozen in dry ice/acetone and lyophilized to a brown residue. This residue contained 10% RDX and 0.32% TNT.

For aquatic toxicological evaluations, the photolysate was used directly as an aqueous solution from the reactors.

When this reactor system is used with chemical photolysis end points of 0.1 ppm TNT ± 100% and 2.3 ppm RDX ± 100%, approximately 4 hours of irradiation time is necessary to produce 1 g of material.

3.5 Identification and sampling of Condensate Wastewater Components

3.5.1 Source

This study entailed the sampling and analysis of wastewaters generated during the production and purification of TNT at Volunteer Army Ammunition Plant (VAAP) in Chattanooga, Tennessee. All wastewaters produced at VAAP are concentrated by evaporation. The condensate of the evaporative process is discharged from the munition facility without the application of further pollution abatement procedures except for pH control and dilution from other industrial operations.

The evaluation of this wastewater, called "condensate wastewater," encompassed the identification of components in the discharge, quantification of the identified components, and development of a representative ratio of discharged components based on sampling studies over a 12-month period. Also incorporated into this sampling program were sampling data taken concurrently by the Naval Surface Weapons Center (NSWC) under the direction of Dr. N. E. Burlinson.

3.5.2 Analytical Methods

The analysis of condensate wastewater samples was performed by gas chromatography (gc). In the early stages of the sampling program, only major components were identified and quantified in the chromatographic profile. As the identifications of minor components were confirmed (through laboratory synthesis of authentic compounds), quantitative data for these components were also generated. In the final stages of the sampling program, glass capillary gc was used to resolve the complexity of condensate mixtures, as described in the appendix.

Condensate samples were analyzed for pH, nitrite, nitrate, and total organic carbon according to the methods described in Section 3.1.2.

Diethyl ether extracts of condensate wastewater that had been dried over anhydrous sodium sulfate and concentrated by rotary evaporation were analyzed under the following gc conditions:

- Instrument: Hewlett-Packard Model 5711 Gas Chromatograph.
- Column: 6' x 1.3 mm ID glass column packed with 10% DC-200 on 80/100 mesh Gas Chrom Q.
- Temperature: 105 to 200° at 4°/min column; 300° detector; on-column injector.
- Flow Rate: 30 ml/min N_2.
- Detection: Flame ionization.

Quantitation was achieved using the internal standard (benzophenone) method and area response compiled by a Hewlett Packard 3380 integrater-recorder. Figure 5 is a typical gc profile of a condensate wastewater extract.

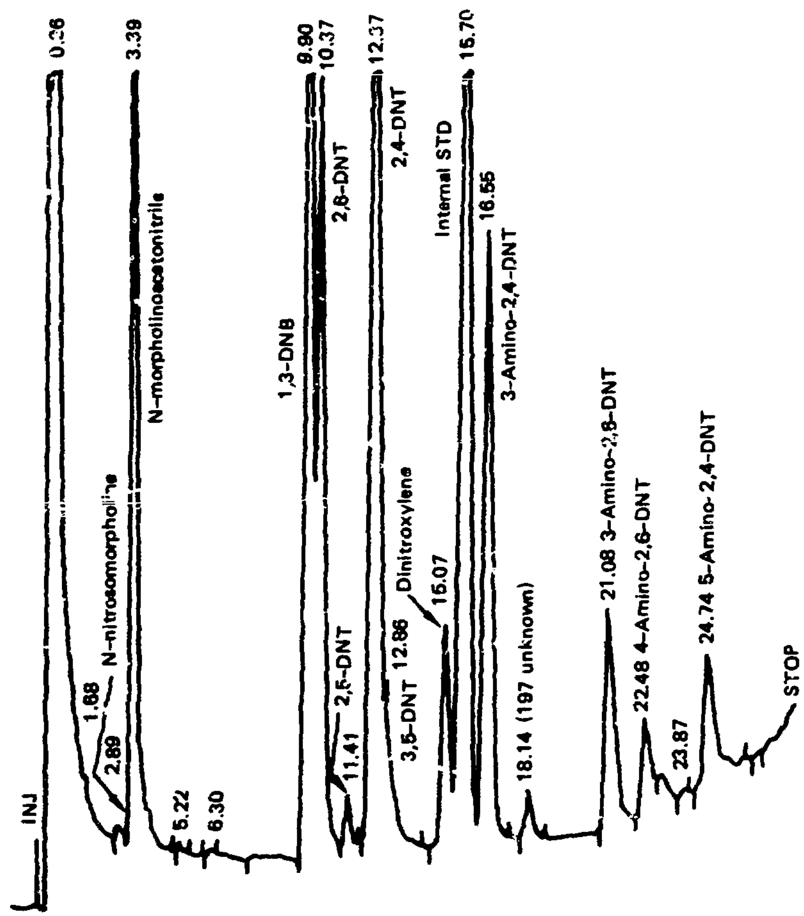
Condensate components were identified using an LKB 9000 gas chromatograph/mass spectrometer (gc/ms) equipped with a PDP-12 computer. Mass spectral data were stored on magnetic tape and recalled to confirm identifications of new samples. A 10% DC-200 column was used to parallel the quantitative analysis reports and to assure that peak identifications in this phase were correct.

3.5.3 Identification of Condensate Components

The organics in condensate wastewater are steam distillates resulting from the evaporative process. These organics are sometimes overshadowed by "red water" components (resulting from the Sellite process) that infrequently arise from a "bumping over" of the pot residue.

Since the components of condensate wastewater are somewhat volatile, gc/ms was used extensively for their identification. Identifications were confirmed by comparing the data derived with those for authentic samples obtained from commercial sources or synthesized at SRI. Exhibit A lists those compounds identified in VAAP condensate wastewater by SRI and NSWC.

Toluene is the basic starting material in the synthesis of TNT, so its presence in discharged wastewaters was not unexpected. The source of N-nitrosomorpholine (I) is unclear. However, morpholine was identified as being an industrial water additive in Betz NA-7 used at VAAP. Because nitrite and acid (yellow water) are generated at various points in the process streams, the potential for N-nitrosation to occur at munition facilities is high (Eq. 1).



RT		AREA	AREA PERCENT
.27		2842919	40.05
.35		3037674	42.8
.41		1054040	14.85
2.89 N-nitros.		298	[illegible] 198
3.39 n.w126		17049	.240 2
5.22		183	.002 578
6.30		142	.002 001
9.90 mDNB		29664	.417 9
10.37 2,6		18305	.257 9
11.41 2,5		984	.013 86
12.37 2,4		31981	.450 6
12.86 3,5		4485	.063 19
15.07 DNX		5242	.073 85
15.70 BOP		26484	.373 1
16.55 197A		14901	.209 9
18.14		1123	.015 82
21.08 197B		6158	.086 76
22.48 197C		1677	.023 63
23.87		107	.001 508
24.74 197D		4388	.061 82

FIGURE 5 GAS CHROMATOGRAPHIC PROFILE OF CONDENSATE WASTEWATER EXTRACT

Exhibit A

COMPOUNDS IDENTIFIED IN CONDENSATE WASTEWATER

Toluene

N-Nitrosomorpholine (I)

N-Morpholinoacetonitrile (II)

2-Nitrotoluene

4-Nitrotoluene

3-Methyl-2-nitrophenol (VI)

5-Methyl-2-nitrophenol (VII)

3-Nitrobenzonitrile

4-Nitrobenzonitrile

1,3-Dinitrobenzene (XIV)

2,[illegible]-Dinitrotoluene

2,5-Dinitrotoluene (XXIII)

2,4-Dinitrotoluene

2,3-Dinitrotoluene (XIX)

3,5-Dinitrotoluene (III)

3,4-Dinitrotoluene

2-Amino-4-nitrotoluene

2-Amino-6-nitrotoluene (XI)

4-Amino-2-nitrotoluene (XII)

3-Amino-4-nitrotoluene (XIII)

1,5-Dimethyl-2,4-dinitrobenzene (XXVII)

1,3,5-Trinitrobenzene (XV)

2,4,6-Trinitrotoluene

2,3,6-Trinitrotoluene (XL)

3-Amino-2,4-dinitrotoluene (XXII)

4-Amino-3,5-dinitrotoluene (IV)

3-Amino-2,6-dinitrotoluene (XX)

4-Amino-2,6-dinitrotoluene

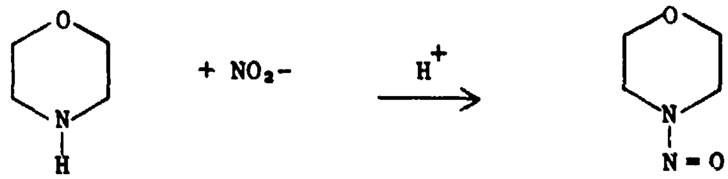
2-Amino-4,6-dinitrotoluene

5-Amino-2,4-dinitrotoluene (IX)

3,5-Dinitroaniline

5-Methyl-2,4-dinitrophenol

2-Amino-3,6-dinitrotoluene (XXXII)



I

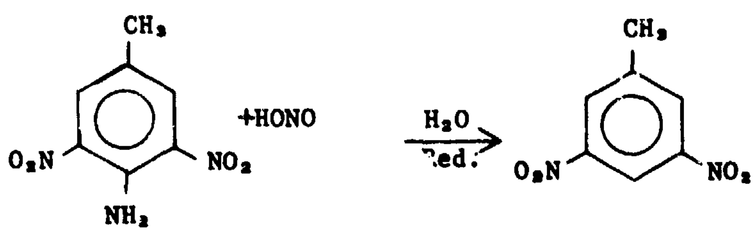
(1)

The source of N-morpholinoacetonitrile is also unclear. However, compounds possessing the structure of II have been reported[8] to be effective algicides, so N-morpholinoacetronitrile may arise from the decomposition of such analogs when used as water additives.

II

(2)

Two of the three isomeric mononitrotoluenes were observed, as were all six isomeric dinitrotoluenes. All these compounds are expected nitration products of toluene, except for 3,5-dinitrotoluene (III), which may arise from the diazotization and decomposition of 4-amino-3,5-dinitrotoluene (IV) in water (Eq. 3) (see Section 3.7).

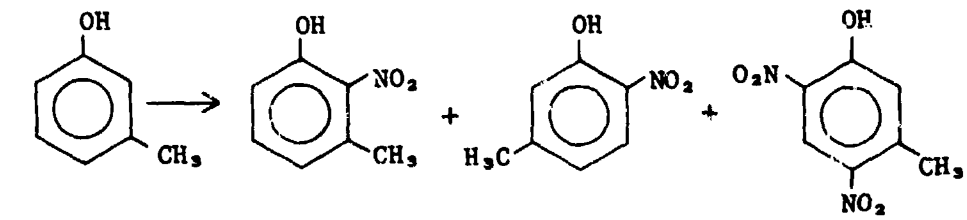


IV

III

(3)

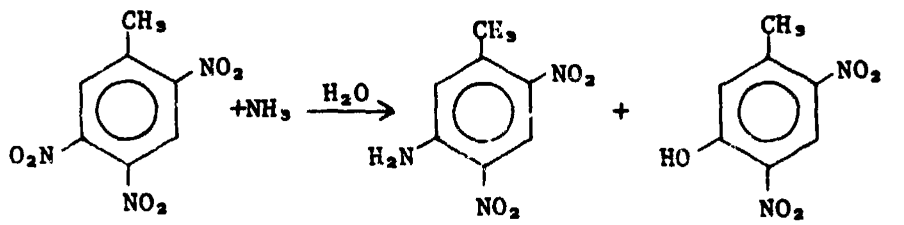
The nitrophenols may result from the nitration of 3-methylphenol (V) to yield 3-methyl-2-nitrophenol (VI) and 5-methyl-2-nitrophenol (VII) (Eq. 4) and a dinitration product, 2,4-dinitro-5-methylphenol



(4)

V VI VII VIII

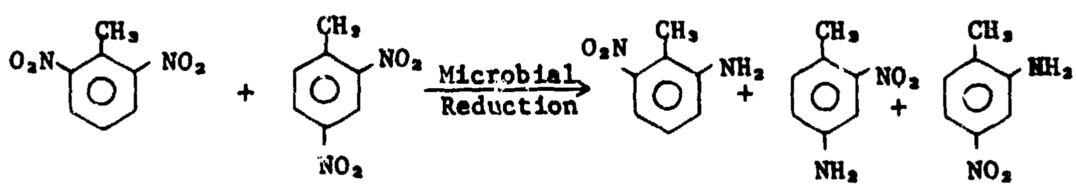
(VIII). Compound VIII was also found in the synthesis of 5-amino-2,4-dinitrotoluene (IX) from 2,4,5-trinitrotoluene (X) and may result in condensate wastewater by this route (Eq. 5).



(5)

X IX

The aminonitrotoluenes [2-amino-6-nitrotoluene (XI), 4 amino-2-nitrotoluene (XII), and 2-amino-4-nitrotoluene (XIII)] may be microbial reduction products of the two major dinitrotoluene isomers, 2,6- and 2,4-dinitrotoluene (Eq. 6). The microbial reduction of aromatic nitro groups has been shown to be a predominant pathway in the biodegradation



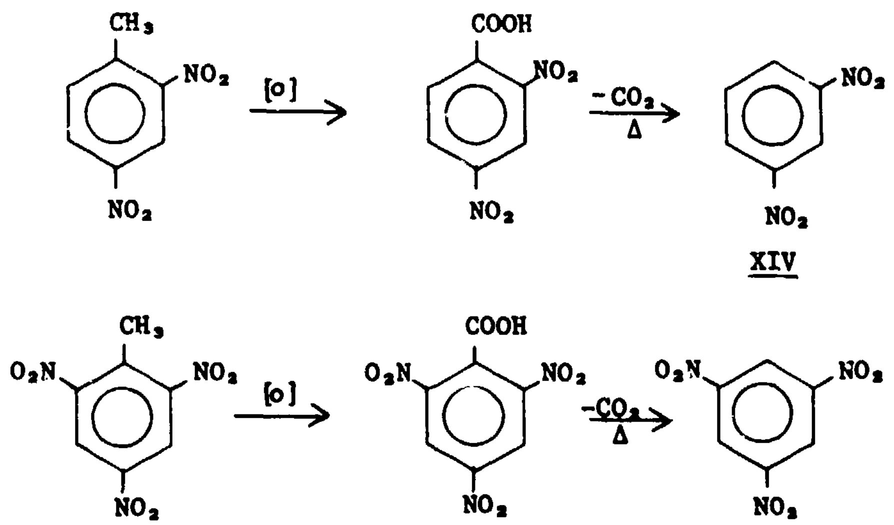
(6)

XI XII XIII

of selected pesticides.[6,7] Although these components were observed in a few samples, their formation may depend on their residence time in settling ponds before their transfer to the evaporators.

The aminodinitrotoluenes may be produced by nucleophilic substitution of ammonia on isomeric trinitrotoluenes. The characteristics of the major TNT isomers resulting from TNT production correlated with those of the major aminodinitrotoluene isomers found in condensate wastewater. Figure 6 summarizes these reactions. Microbial reduction does not appear to be responsible for these compounds (except possibly for 2-amino-4,6-dinitrotoluene) since their distribution in the sampling program was predictable.

Two nitrated benzenes were observed--1,3-dinitrobenzene (XIV) and 1,3,5-trinitrobenzene (XV). These compounds may arise from the nitration of benzene or through decarboxylation of their corresponding acids (Eq. 7).



XIV

(7)

XV

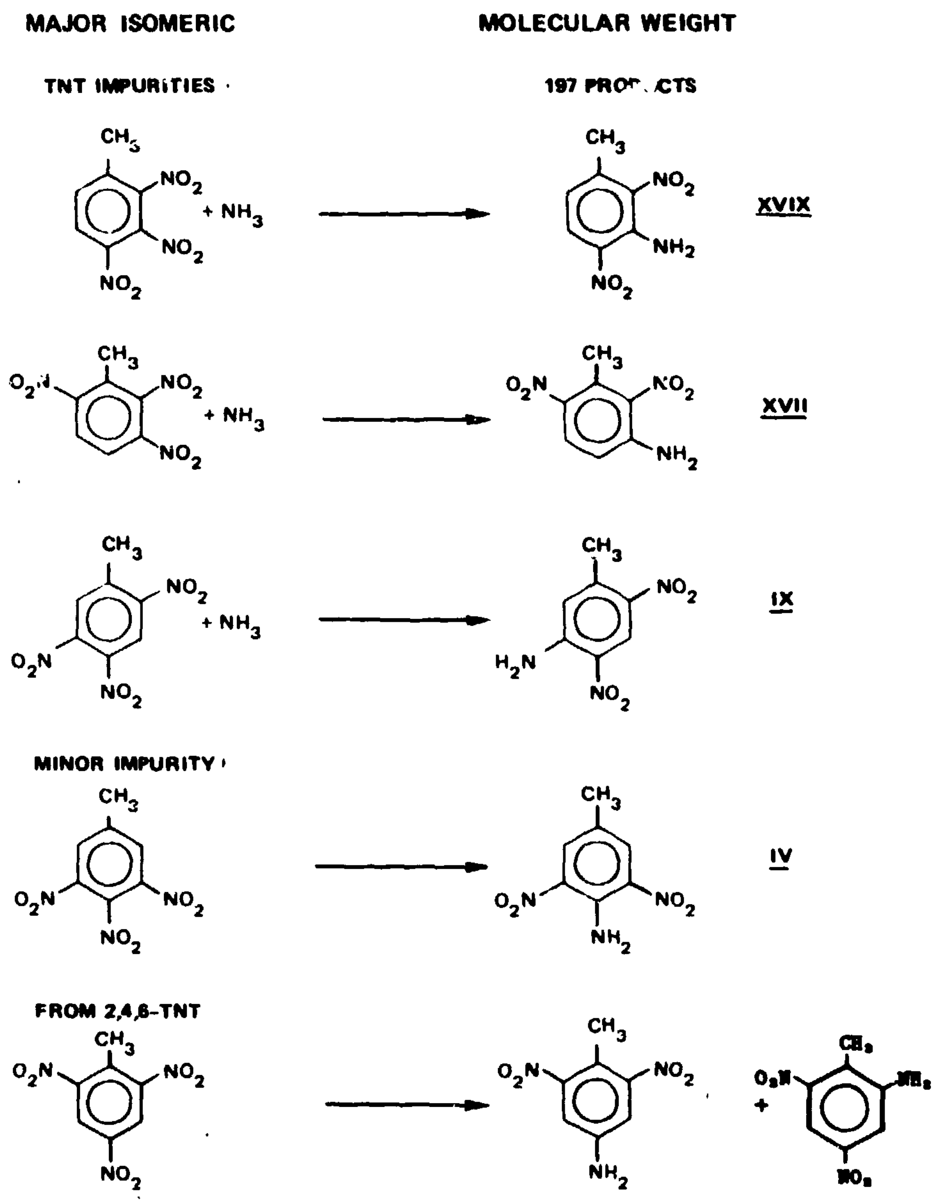


FIGURE 6 POSSIBLE ROUTE OF FORMATION OF AMINODINITROTOLUENES IN CONDENSATE WASTEWATER

Except for the effect of nitrating reagents on water additives, finding many nitroaromatics in the condensate discharge was not surprising. Higher specifications for the purity of toluene used in the process may reduce the formation and outflow of several products, but the majority of the products probably are unique to the present manufacturing conditions and may only be eliminated by major changes in the manufacturing and purification processes.

3.5.4 Sampling Data

The data reported here are the combination of analyses performed by SRI and NSWC from 25 February 1976 to 22 January 1977. Samples were collected as described in Section 3.1.2. The SRI data are listed in Table 8, and the data from NSWC are listed in Table 9 and reflect the observed concentrations (mg/liter or ppm) of those compounds listed in Exhibit A.

Mass spectroscopy was used to quantify the aminonitrotoluenes because these components were underlying peaks of major components. Using selective ion monitoring, we found that 2-amino-4-nitrotoluene, 4-amino-2-nitrotoluene, and 2-amino-6-nitrotoluene were present in Sample 61 at 0.[illegible] ppm, 0.08 ppm, and 0.02 ppm, respectively, and in Sample 65 at 0.02 ppm, 0.03 ppm, and 0.02 ppm, respectively.

Table 10 lists the values for pH, nitrite, nitrate, and total organic carbon obtained for the samples listed in Table 8.

3.6 Establishment of Representative Discharge Ratios for Condensate Components

The sampling data were highly variable, showing no consistent pattern of component outflows by visual inspection or by mean value of determinations. Since the objective was to determine a representative distribution of component concentrations in a discharge, we applied cluster analysis of the data points using a computer program developed at SRI for handling multivariate data.

Table 8

COMBINED VAAP CONDENSATE SAMPLING DATA FROM SRI
(Milligrams per Liter)

SRI Sample No.	Date	N-Nitrosomorpholine	N-Morpholinoacetonitrile	2-Nitrotoluene	4-Nitrotoluene	1,3-Dinitrobenzene	2,6-Dinitrotoluene	2,5-Dinitrotoluene	2,4-Dinitrotoluene	2,3-Dinitrotoluene	3,5-Dinitrotoluene	3,4-Dinitrotoluene	1,3-Dimethyl-2,4-dinitrobenzene	4-Methyl-3-nitrophenol	5-Methyl-2-nitrophenol	2-Amino-4,6-Dinitrotoluene	2,4,6-Trinitrotoluene	4-Amino-3,5-dinitrotoluene	3-Amino-2,6-dinitrotoluene	4-Amino-2,6-dinitrotoluene	5-Amino-2,4-dinitrotoluene
20	2/25	-	-	-	-	[illegible]	7.3	.	[illegible]	-	•	0.5	•	•	•	-	-	•	-	•	-
25	3/5	-	-	+	+	[illegible]	0.5	[illegible]	[illegible]	-	•	0.5	•	•	•	+	-	•	-	+	-
26	3/9	0.3	0.7	0.05	0.02	4.6	1.9	0.4	[illegible]	-	0.16	[illegible]	.16	•	•	1.4	-	.02	1.0	0.5	.3
27	3/17	-	+	+	+	6.1	3.0	.4	1..7	+	•	-	•	•	•	+	-	•	+	+	+
28	3/26	-	+	-	-	5.2	1.0	0.4	12.4	+	•	0.7	•	∘	•	+	-	•	+	+	+
29	3/30	0.1	+	0.04	0.04	4.3	[illegible]	.6	11..	.4	0.49	0.6	.18	•	•	1.0	-	0.0	0.5	.1	0.2
56	3/31	-	+	-	-	3.5	4.4	0.3	20.0	-	•	0.6	•	•	•	+	-	•	+	+	-
31	4/26	+	+	-	-	[illegible]	6.5	0.4	17.8	+	•	1.7	•	•	•	+	-	•	+	+	+
32	4/28	+	1.2	0.02	0.02	3.6	7.0	0.5	11..	.6	0.52	[illegible]	.10	•	•	1.0	+	0.05	0.9	0.3	0.5
63	4/28	-	+	-	-	2.8	3.3	0.4	[illegible]	0.3	•	0.3	•	•	•	+	1.1	•	+	1.1	+
33	5/5	0.05	0.4	0.04	0.07	1.5	14.9	0.2	22.4	[illegible]	.58	0.6	.06	0.11	0.013	0.4	-	[illegible]	[illegible]	0.3	0.3
34	5/22	-	+	-	+	1.3	14.3	0.4	26.5	0.6	•	0.7	•	•	•	+	-	•	+	+	+
35	5/14	0.09	0.8	0.02	0.03	1.1	11.8	0.4	24.5	.4	.52	1..	.15	0.007	0.006	0.9	-	0.05	0.6	0..	0.2
36	5/27	-	+	-	-	1.4	5.4	0.1	10.7	2.0	•	0.5	•	•	•	+	-	•	+	+	+
85	5/27	+	+	+	+	0.4	7.4	0.3	16.8	[illegible]	•	0.7	•	•	•	+	1..	•	+	0.1	+
37	6/4	-	+	-	-	1.6	7.9	0.2	14.7	0..	•	[illegible]	•	•	•	+	+	•	+	+	+
38	6/11	-	+	-	-	1.5	7.3	0.1	14.0	+	•	0.5	•	•	•	+	+	•	+	-	-
95	6/23	-	-	-	-	2.0	11.3	0.5	48.6	0.4	•	0.3	•	•	•	+	3.4	•	+	0.4	+
39	6/22	0.06	+	-	-	0.6	7.2	-	11.2	0.4	0.44	0.4	0.10	•	•	0.7	1.7	0.03	0.3	0.3	0.3
40	7/2	+	+	-	-	0.8	3.3	0.2	2.9	0.6	+	0.1	0.01	•	•	+	0.1	+	-	0.9	-
41	7/13	+	+	-	-	0.7	3.5	0.3	9.6	0.6	•	0.4	•	•	•	+	0.5	•	-	-	-
42	7/15	+	+	-	-	0.7	3.8	-	6.6	0.2	•	-	•	•	•	+	0.9	•	+	-	-
43	8/9	+	+	-	-	2.1	2.9	-	4.2	+	•	0.2	•	•	•	+	0.4	•	+	+	+
44	8/16	+	+	-	-	1.8	2.7	0.5	1.4	0.5	0.14	0.2	0.14	•	•	+	-	0.02	+	0.3	-
45	8/20	+	+	-	-	0.7	2.3	0.4	1.3	+	0.22	0.3	0.05	•	•	0.5	+	0.21	+	-	-
46	9/13	-	-	-	-	2.1	2.9	0.1	6.4	+	0.83	[illegible]	0.33	•	•	1.5	-	0.06	-	-	-
46A	9/10	-	-	-	-	1.8	3.3	0.1	7.9	+	•	0.2	•	•	•	1.6	+	•	+	-	-
46B	9/9	-	-	-	-	1.7	2.8	0.1	6.6	-	•	0.3	•	•	•	1.5	+	•	-	-	-
46C	9/8	+	+	-	-	1.8	3.0	0.1	6.5	-	•	0.2	•	•	•	1.5	-	•	-	-	-
47	9/14	-	-	-	-	1.6	2.8	0.15	7.5	+	0.70	0.2	0.26	•	•	1.7	-	0.03	-	-	-

Table 8 (Concluded)

SRI Sample No.	Date	N-Nitrosomorpholine	N-Morpholinoacetonitrile	2-Nitrotoluene	4-Nitrotoluene	1,3-Dinitrobenzene	2,6-Dinitrotoluene	2,5-Dinitrotoluene	2,4-Dinitrotoluene	2,3-Dinitrotoluene	3,5-Dinitrotoluene	3,4-Dinitrotoluene	1,5-Dimethyl-2,4-dinitrobenzene	3-Methyl-2-nitrophenol	5-Methyl-2-nitrophenol	3-Amino-2,4-Dinitrotoluene	2,4,6-Trinitrotoluene	4-Amino-3,5-dinitrotoluene	3-Amino-2,6-dinitrotoluene	4-Amino-2,6-dinitrotoluene	5-Amino-2,4-dinitrotoluene
48	9/15	-	-	-	-	1.9	4.9	0.13	8.5	+	0.44	0.1	0.20	*	*	1.4	-	-	+	-	-
49	9/16	-	-	-	-	1.4	2.9	0.1	7.3	+	0.82	0.1	0.39	*	*	1.0	-	+	-	-	-
50	9/17	0.06	0.3	-	-	1.4	2.9	-	7.9	+	0.59	0.2	0.30	-	-	1.0	-	+	0.2	0.1	0.1
51	9/21	0.01	0.08	-	-	1.0	1.7	-	2.0	-	0.43	0.2	0.45	0.010	0.021	0.3	-	0.04	0.1	0.2	0.1
52	9/23	0.01	0.9	-	-	0.8	1.8	-	2.5	-	0.25	-	0.37	0.008	0.027	0.4	-	0.02	0.1	0.1	0.1
53		-	0.5	-	-	1.0	2.6	-	4.8	+	0.39	-	0.49	-	-	0.9	-	0.02	0.2	0.1	0.2
54	9/24	0.03	0.5	-	-	0.9	3.5	-	3.5	-	[illegible]	-	0.36	0.010	0.049	0.5	-	0.02	0.05	0.2	0.2
55	9/30	0.03	0.1	-	-	0.5	1.8	-	3.2	-	0.38	-	0.19	0.014	0.010	0.4	-	0.03	0.01	0.03	0.08
56A	10/1	0.01	0.02	-	-	0.2	0.9	-	1.3	-	0.22	-	0.10	-	-	0.1	-	-	-	-	-
57	10/7	0.2	0.8	-	-	2.5	2.5	-	3.4	+	0.46	-	0.29	0.011	0.018	1.5	-	0.07	0.8	0.2	0.6
58	10/6	0.1	0.5	-	-	1.8	2.0	-	3.0	-	0.52	-	0.43	0.019	0.024	1.4	-	0.05	0.4	0.2	0.4
59	10/9	0.3	1.6	-	-	2.8	2.2	-	3.1	-	0.47	-	0.28	0.028	0.032	1.5	-	0.08	1.8	0.4	2.0
60	10/15	0.1	1.6	-	-	3.6	2.6	-	3.4	*	0.47	-	0.30	*	*	1.5	-	0.04	1.2	0.7	1.7
61	10/22	0.1	1.0	-	-	3.8	3.0	-	3.2	*	0.47	-	0.44	0.012	0.020	1.7	-	0.05	3.8	0.3	0.4
50	4/7	0.2	0.3	0.07	0.03	3.3	2.4	0.2	9.2	*	+	0.4	0.17	0.034	0.016	1.0	-	-	0.8	0.3	0.3
62	10/20	0.07	0.4	-	-	3.5	2.1	0.1	2.2	+	0.45	-	0.71	*	*	1.9	-	0.31	4.4	2.3	17.5
63	10/27	0.07	1.9	-	0.01	3.6	1.6	0.04	3.0	-	0.41	-	0.53	-	-	1.7	-	0.13	0.7	0.4	0.7
65	10/27	0.06	2.0	+	0.01	3.6	1.6	0.09	3.0	-	6.48	-	0.56	0.010	0.015	1.7	-	0.13	0.7	0.2	10.7
66	10/28	0.06	0.9	0.03	0.02	1.8	0.9	0.01	2.3	-	+	-	0.23	0.010	0.044	1.1	-	0.03	0.5	0.07	0.3
67	10/24	0.08	0.8	0.02	0.01	1.8	1.7	0.03	2.8	+	+	-	0.15	0.005	0.032	1.3	-	0.02	0.6	0.03	0.2
69	11/16	0.14	+	0.02	0.01	-	0.1	-	0.2	-	-	-	-	-	-	+	0.2	-	0.07	-	-
70	11/18	0.06	0.14	0.02	0.02	-	0.06	-	0.04	-	-	-	-	-	-	0.03	-	-	-	-	-
71	1/22	0.24	0.98	0.12	0.15	1.78	0.98	0.01	2.85	+	0.25	0.05	0.24	-	-	1.52	-	0.04	0.80	0.22	0.54
72	1/22	0.29	1.14	0.14	0.17	1.24	0.99	0.01	2.85	+	0.34	0.03	0.35	-	-	1.44	-	0.04	0.78	0.28	0.50

* Not determined.

\- Not detected.

\+ Detected but not quantified.

Table 9

[illegible] AAP CONDENSATE SAMPLING DATA FROM NSWC
Milligrams per Liter

Date	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1[illegible] 1	1[illegible]/6	1[illegible]/7	10/8	10/1[illegible]	10/20	10/22	10/27	10/28	10/29
Toluene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	0.1	0.02	0.1	0.2	0.2
N-Nitrosomorpholine	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	.10	0.05	0.10	0.03	0.02	0.01
N-Morpholine-acetonitrile	[illegible]	[illegible]	[illegible]	1.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.4	1.	1.[illegible]	1.[illegible]	[illegible].5	0.6	0.9	0.5	0.9
2-Nitrotoluene	[illegible]	[illegible]	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	-	.001	-	0.002	0.01	0.001	-
4-Nitrotoluene	.1	[illegible]	[illegible]	.1	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.1	.1	[illegible]	[illegible]	-	.00[illegible]	-	0.005	0.00[illegible]	0.006	0.003	0.003	0.003
1,3-Dinitrobenzene	[illegible]	1	[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1	[illegible]	.1	1.[illegible]	[illegible]	[illegible]	[illegible]	4	4	1	0.5	0.6
2,6-Dinitrotoluene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3	[illegible]	0.9	2
2,[illegible]-Dinitrotoluene	[illegible]	[illegible]	[illegible]	.1	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	[illegible]	-	.01	0.01	0.07	[illegible]	0.01	0.02
2,[illegible]-Dinitrotoluene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1	4	4	4	[illegible]	3	3	2	3
[illegible],[illegible]-Dinitrotoluene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.1	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.01	0.01	0.01
3,[illegible]-Dinitrotoluene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	.01	[illegible]	0.01	0.2	0.08	0.04
3,4-Dinitrotoluene	0.[illegible]	[illegible]	[illegible]	.1	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	-	.001	-	0.01	0.01	-	0.01
1,3,5-Trinitrobenzene	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	[illegible]	-	-	-	-
2,3,6-Trinitrotoluene	-	-	-	[illegible]	[illegible]	1.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	-	-	[illegible]	-	-	0.05
2,4,6-Trinitrotoluene	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	-	-	-	-	-	-	-	-
3-Amino-2,4-dinitrotoluene	1	.6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1	[illegible]	1	1	1	[illegible]	0.3	[illegible].6
4-Amino-3,5-dinitrotoluene	[illegible]	.21	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	.1	[illegible]	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.6	[illegible]	0.40	0.08	0.1[illegible]
2-Amino-3,6-dinitrotoluene	-	-	-	[illegible]	-	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-	-	0.01
3-Amino-2,6-dinitrotoluene	0.90	[illegible]	-	[illegible]	.5	[illegible]	[illegible]	[illegible]	.1	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	4.[illegible]	[illegible].90	0.40	[illegible]
4-Amino-2,6-dinitrotoluene	0.30	[illegible].70	[illegible]	[illegible]	.1	[illegible]	.1	.1	[illegible]	0	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.[illegible]	[illegible].1
2-Amino-4,6-dinitrotoluene	0.34	0.[illegible]	.001	[illegible]	.1	.1	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible].1	[illegible]	[illegible]	-	1[illegible]	0.[illegible]	0.[illegible]1	[illegible]
5-Amino-2,4-dinitrotoluene	0.3	0.[illegible]	[illegible]	[illegible]	.1	[illegible]	[illegible]	[illegible]	.1	.1	.1	[illegible]	[illegible]	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	1	[illegible]	0.[illegible]	[illegible]
2-Amino-4-nitrotoluene	-	-	-	-	-	[illegible]	[illegible]	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	.[illegible]	[illegible]	-	-	-		-	-
2-Amino-6-nitrotoluene	-	-	-	-	-	.[illegible]	[illegible]	[illegible]	.1	[illegible]	.1	[illegible]	[illegible]	[illegible]	.1	[illegible]	[illegible]	[illegible].1	-	-	.1[illegible]	-	[illegible].5[illegible]
4-Amino-2-nitrotoluene	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	.1[illegible]	-	-	-	-	[illegible]	-	-	-
2-Nitro-3-methylphenol	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.10[illegible]	.1[illegible]
3-Amino-4-nitrotoluene	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		-	-	-	[illegible]	[illegible]	[illegible]	-	-
2,4-Dinitro-5-methylphenol	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-		.1[illegible]	[illegible]	-	[illegible]	.10[illegible]	.1[illegible]	-	[illegible]
3,5-Dinitroaniline	-	-	-	-	-	-	[illegible]	.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	0.[illegible]	.1	[illegible]	-	-
4-Nitrobenzonitrile	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	-	-	-	[illegible]	[illegible]0	-	-
3-Nitrobenzonitrile	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	-	-	.01	[illegible].009	[illegible].1	-
Unknown M/e = 197	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	-	[illegible]	-		-	-
Unknown M/e = 128	0.005	-	0.00[illegible]	0.010	-	.[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	.1	[illegible].01	-	[illegible]	.01	[illegible].01	-
Unknown M/e = 164	-	-	-	-	-	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]	-	-		-	.7	[illegible].1	[illegible]

- Not detected + Detected but not quantified

Table 10

COMBINED WAAP CONDENSATE VALUES FOR pH, NITRITE, NITRATE, AND TOC

[illegible] No.	Date	pH	Nitrite	Nitrate	TOC
[illegible]	[illegible]	[illegible]	1690	65	•
[illegible]	3/3	8.58	24	•	34
[illegible]	3/9	8.79	19	•	30
[illegible]	3/17	8.73	360	•	29
[illegible]	[illegible]	[illegible]	30	•	•
[illegible]	3/30	8.99	155	•	28
[illegible]	[illegible]	8.1	18	[illegible]	28
31	[illegible]	8.17	9	16.[illegible]	25
[illegible]	4/28	8.11	21	•	34
[illegible]	[illegible]	8.10	19	52	25
33	[illegible]	8.80	•	•	46
34	[illegible]	8.75	11.	•	42
35	5/14	8.80	104	•	39
36	[illegible]	8.74	105	•	•
[illegible]	5/27	9.45	14	[illegible]	•
37	6/4	8.40	184	6 1	•
38	[illegible]	8.71	[illegible]	5.2	9
[illegible]	6/23	9.11	2310	17.2	•
39	[illegible]	8.87	231	3.7	•
40	7/2	9.00	160	1.7	•
41	7/15	8.81	6	470	10
42	7/13	8.75	4	•	17
43	8/9	9.01	4.9	•	10
44	8/16	9.20	[illegible]	•	14
45	8/20	8.35	2.7	5.4	8
46	9/13	8.44	15	68	68
46A	9/10	8.86	4.7	8.5	16
46B	9/9	9.14	4.5	7.3	14
46C	9/8	9.13	5.2	21.4	18
47	9/14	9.05	4.9	7.2	14
48	9/15	8.90	4.7	8.0	17
49	9/16	9.26	2.2	5.0	14
50	9/17	9.13	2.2	4.2	15
51	9/21	9.17	0.4	8.8	11
52	9/23	9.21	1.1	18	16
53		8.95	1.3	5	14
54	9/24	9.01	2.9	27	22
55	9/30	8.93	1.0	10.8	13
56L	10/1	9.09	0.2	4.0	9
57	10/7	8.94	11	62	32
58	10/6	9.16	7.5	10	14
59	10/8	8.99	31	1720	306
60	10/15	9.13	11.3	11.5	16
61	10/22	9.18	16.8	11.5	20
30	4/7	7.87	26.7	50	25
62	10/20	8.88	33.5	•	2733
63	10/27	9.20	23	50	24
65	10/27	8.98	24.6	19	23
66	10/28	9.35	17	64	20
67	10/24	8.37	20	64	23
69	11/16	9.22	23.1	70	114
70	11/18	8.02	1	5	4
71	1/22/77	8.82	19.6	24	17
72	1/22/77	8.39	19.7	25	17

Essentially, this clustering program is a multivariate extension of the process of graphing data cases with two variables and pictorially dividing the data into clusters on the basis of proximity. The mean for each of the two variables is computed and represented graphically. The data case furthest from the mean starts a second cluster, the first cluster containing all the remaining data points. The criterion for allocation of all further cases is the total error--the sum of distances squared from each data case to the cluster mean of the cluster to which it is assigned. This procedure of minimizing total error is designed to minimize distances within clusters and maximize distances between clusters.

Each data case from the first cluster is sequentially moved into the second cluster, which initially contained only one case. The cluster means and total error of the two clusters are computed after the move, and the case is returned to the first cluster After total err is computed for all data cases, the data case, if any, for which total error is minimum and less than the total error with only one case in the second cluster is now assigned to the second cluster. Data cases are added to the second cluster in this manner. When the total error can no longer be reduced by addition of a data case to the second cluster, the point furthest from its cluster mean is designated to start a third cluster. All data cases from the first and second cluster are tested for reduction of total error by being moved into one of the two other clusters, as above. This process is repeated until some preselected maximum number of clusters has been obtained. The number of clusters actually used for analysis is choosen by the program user.

Using 17 variables (major components plus pH, nitrite, nitrate, and TOC) from 45 condensate samples in Table 8, the clustering analysis was performed. At five clusters, the data were divided into two major clusters consisting of 18 samples each and three minor clusters. Table 11 shows the representative percentage of the distribution of components described in each of the major clusters and the average percentage of distribution determined from the two clusters.

Table 11

RELATIVE PERCENTAGES OF CONDENSATE COMPONENTS DERIVED FROM COMPUTER CLUSTERS

Condensate Component	Cluster 1 ppm	Cluster 1 %	Cluster 2 ppm	Cluster 2 %	Average (%)
1,3-Dinitrobenzene	1.09	9.1	2.9	11.2	10.2
2,6-Dinitrotoluene	2.66	22.2	5.98	23.1	22.7
2,5-Dinitrotoluene	0.1	1	0.3	1	1.0
2,4-Dinitrotoluene	5.3	44.2	13.7	52.9	48.6
3,4-Dinitrotoluene	0.2	1.7	0.54	2.1	1.9
2,3-Dinitrotoluene	0.4	3.3	0.53	2.0	2.7
2,4,6-Tinitrotoluene	0.5	4.2	0.54	2.1	3.2
4-Amino-2,6-dinitrotoluene	0.34	2.8	0.26	1	1.9
N-Nitrosomorpholine	0.1	1	0.13	0.5	0.7
N-Morpholinoacetonitrile	0.24	2	0.24	1	1.5
3-Amino-2,4-dinitrotoluene	0.78	6.5	0.31	1.2	3.9
3-Amino-2,6-dinitrotoluene	0.14	1.2	0.27	1	1.1
5-Amino-2,4-dinitrotoluene	0.15	1.3	0.18	0.7	1.0

As more data became available for the minor components, these data were combined with the data provided by NSWC (Table 9), and the U.S. Army Medical Bioengineering Research and Development Laboratory developed a representative percentage of distribution of condensate components, as shown in Table 12. This was accomplished by taking the 90th percentile concentration of those compounds that appeared in at least 10% of the samples and dividing that number by the sum of the concentrations of all other comp ents. For those compounds that did not have a non-zero 90th percentile concentration, a mean non-zero concentration was determined and it was then divided by the sum of the concentrations of the other components.

Table 12

90TH PERCENTILE CONCENTRATIONS AND RELATIVE CONCENTRATIONS DETERMINED FOR CONDENSATE COMPONENTS

Condensate Component	90th Percentile Concentration (mg/liter)	Relative Concentration (%)
Toluene	0.200	0.590
2-Nitrotoluene (NT)	0.030	0.089
4-Nitrotoluene	0.100	0.295
3-Nitrobenzonitrile*	0.013	0.035
4-Nitrobenzonitrile*	0.009	0.027
2-Amino-4-NT	0.033	0.097
2-Amino-6-NT*	0.010	0.0[illegible]
3-Amino-4-NT*	0.027	0.080
3-Methyl-2-nitrophenol	0.012	0.035
5-Methyl-2-nitrophenol	0.032	0.094
1,3-Dinitrobenzene (DNB)	4.000	11.803
2,3-Dinitrotoluene (DNT)	0.400	1.180
2,4-DNT	14.700	43.377
2,5-DNT	0.400	1.180
2,6-DNT	7.300	21.541
3,4-DNT	0.500	1.475
3,5-DNT	0.520	1.534
3,5-Dinitroaniline*	0.058	0.171
1,5-Dimethyl-2,4-DNB (DNX)	0.390	1.151
2-Amino-3,6-DNT	0.030	0.089
2-Amino-4,6-DNT	0.020	0.059
3-Amino-2,4-DNT	1.500	4.426
3-Amino-2,6-DNT	1.200	3.541
4-Amino-2,6-DNT	0.600	1.770
4-Amino-3,5-DNT	0.200	0.590
5-Amino-2,4-DNT	0.700	2.066
2,4-Dinitro-5-methylphenol*	0.085	0.251
1,3,5-Trinitrobenzene (TNB)*	0.153	0.451
2,3,6-Trinitrotoluene (TNT)*	0.268	0.791
2,4,6-TNT	0.400	1.180

* Compounds were not present in 10% of the samples. Value given represents the mean of the non-zero values.

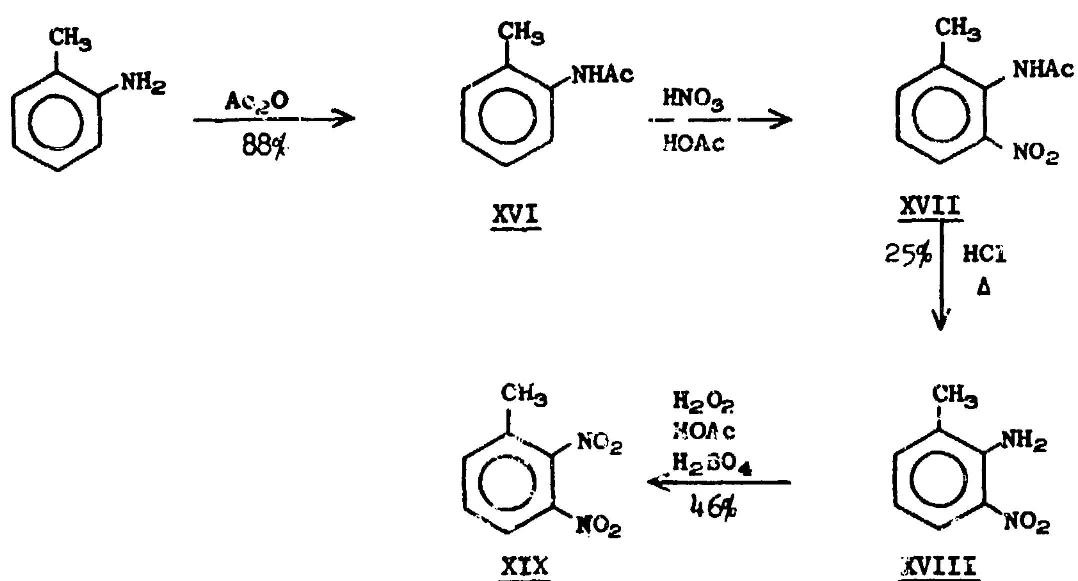
The data in Table 12 represent the relative distribution of components to be expected in a condensate discharge at VAAP. Although these data are derived from a larger data base than those used in the cluster analysis, the component distribution patterns are similar, verifying the reliability of the methods.

3.7 Methods for the Synthesis of Condensate Components

Of the 33 compounds identified in condensate wastewater, many could not be obtained from commercial sources. Therefore, methods were developed to synthesize these compounds in sufficient quantities for the mammalian and aquatic toxicological studies.

The procedures and synthetic routes for the preparation of both intermediate and final products are detailed in the following sections.

3.7.1 Preparation of 2,3-Dinitrotoluene (XIX)



O-Acetotoluimide (XVI)

Acetic anhydride (3000 g, 29.4 mol) was added to a mixture of 3000 g (28.0 mol) of o-toluidine, 500 ml of water, and 1000 ml of acetic acid at 40 to 45° over a 1-hr period with ice/water cooling. The reaction mixture was poured into 20 liters of cold water to precipitate the product, which was removed by filtration and dried to yield 3680 g of material (88% yield).

N-Acetyl-2-Amino-3-Nitrotoluene (XVII)

O-Acetotoluimide (960 g, 6.4 mol) was added to a mixture of 3600 g of 90% nitric acid and 1200 g of glacial acetic acid at 5 to 10°. The reaction mixture was stirred at 25° with ice/water cooling for 3 hr and then poured into 8 liters of ice/water to precipitate the product. The product was removed by filtration but was dried only with difficulty; therefore, it was slightly wet when used in the next step.

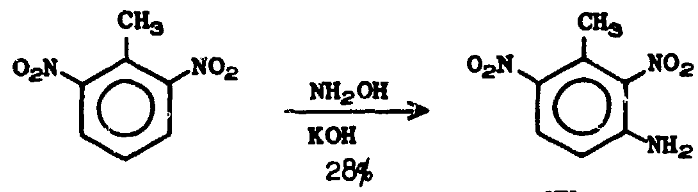
2-Amino-3-Nitrotoluene (XVIII)

Half the product obtained from the nitration of O-acetotoluimide was refluxed in 4 liters of hydrochloric acid for 7 hr, during which time an additional 600 ml of hydrochloric acid was added. The hot reaction mixture was poured into 20 liters of cold water to precipitate the product, which was removed by filtration and dried. Recrystallization from hot methanol yielded 123 g of product, a 25% combined yield for nitration and hydrolysis.

2,3-Dinitrotoluene (XIX)

2-Amino-3-nitrotoluene (400 g, 2.6 mol) was added in small portions to a mixture of 2000 ml of acetic acid, 25 ml of sulfuric acid, and 600 ml of 90% hydrogen peroxide at 80 to 90°. The reaction exotherm maintained the temperature without external heating. After the exotherm had ceased, 350 ml of 30% hydrogen peroxide was added, and the reaction was heated to 80 to 90° for 3 hr more. The mixture was then cooled and poured into 8 liters of cold water. The product was removed by filtration and recrystallized from methanol; 220 g, 46% yield.

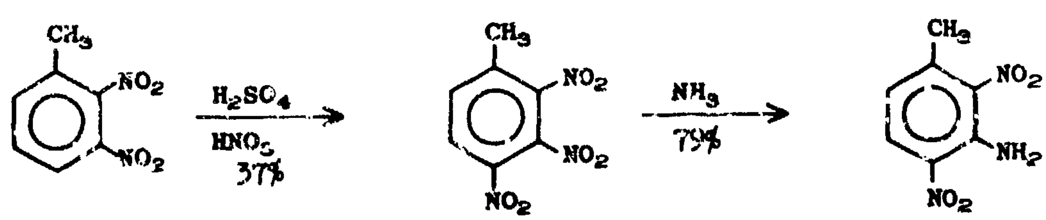
3.7.2 Preparation of 3-Amino-2,6-Dinitrotoluene (XX)



XX

A mixture of 500 g (275 mmol) of 2,6-dinitrotoluene and 50.0 g (720 mmol) of hydroxylamine hydrochloride in 1100 ml of 95% ethanol was placed in a 5-liter flask fitted with a mechanical stirrer, addition funnel, and thermometer. This mixture was cooled to 5°, and 500 ml of methanol saturated with 85% KOH was added dropwise over a 1.5-hr period while the temperature was kept at 5 to 10°. The color of the reaction mixture turned from white to blue-grey to reddish brown as the base was added. When the addition of base was completed, 3000 ml of water was added, causing precipitated KCl to dissolve and an organic product to precipitate. After 1 hr, the product was collected by filtration, washed with water, and dried under vacuum over P_2O_5; wt, 20.4 g. Recrystallization from a hexane-chloroform mixture after charcoal treatment gave 15.05 g of a yellow crystalline solid that was identified as 3-amino-2,6-dinitrotoluene by its nmr spectrum; yield, 28%.

3.7.3 Preparation of 3-Amino-2,4-Dinitrotoluene (XXII)



XXI

XXII

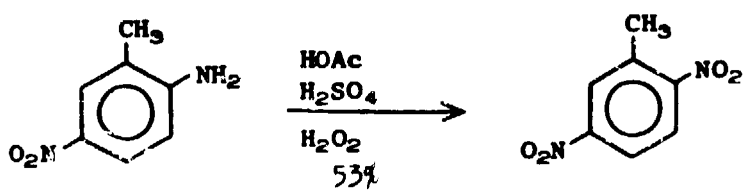
2,3,4-Trinitrotoluene (XXI)

Sulfuric acid (96%, 3000 ml) was cooled to 10°, and 1100 ml of 90% nitric acid was added over a 30-min period while the temperature was allowed to rise to 50°. The mixture was heated to 80°, and 383 g (2.1 ml) of 2,3-dinitrotoluene was added in small portions at such a rate that the temperature remained at 80 to 83° without external heating or cooling. After the addition was complete, the mixture was heated to 95° for an additional hour. The mixture was cooled and poured into 9 liters of ice/water. The precipitated product was removed by filtration, dried, recrystallized from 1800 ml of methanol, and recrystallized from 1200 ml of methanol; 177 g, 37% yield.

3-Amino-2,4-Dinitrotoluene (XXII)

Aqueous ammonia (70 ml) was added to a solution of 25 g (0.11 mmol) of 2,3,4-trinitrotoluene in 250 ml of absolute ethanol at 65°; the addition rate was regulated so as to maintain the 65° reaction temperature without external heating or cooling. After the exotherm had ceased, the reaction was refluxed slowly for 1 hr and then cooled to 5°. The product was removed by filtration; 17.2 g, 79% yield.

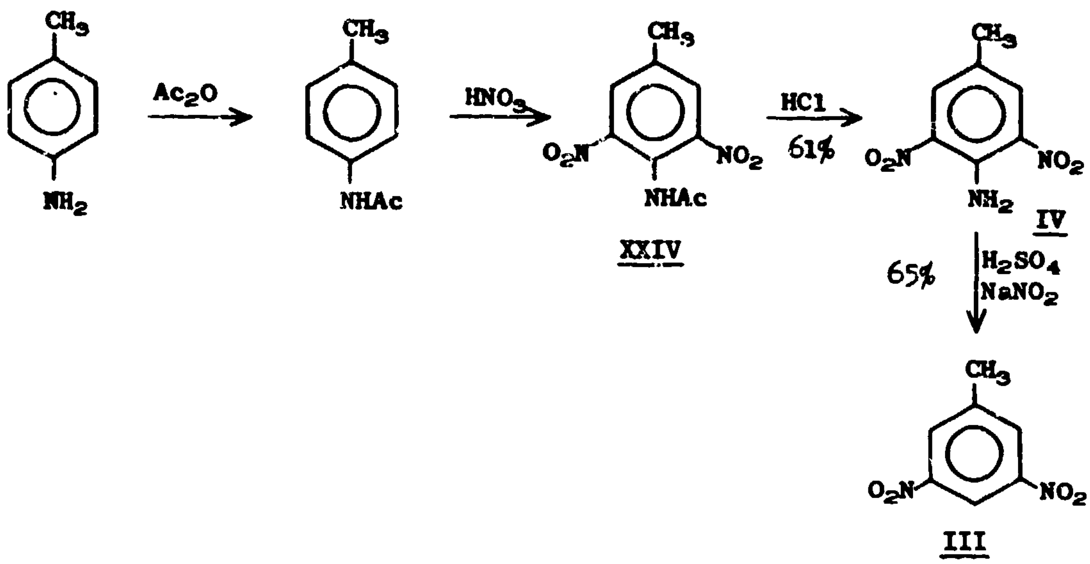
3.7.4 Preparation of 2,5-Dinitrotoluene (XXIII)



XXIII

Into a 12-liter three-neck flask fitted with a thermometer, mechanical stirrer, and drying tube were placed 3600 ml of glacial acetic acid, 100 ml of conc. H_2SO_4, and 500 ml of 30% H_2O_2. The flask was heated to 68°, and 200 g of 2-amino-5-nitrotoluene in 2000 ml of hot glacial acetic acid was added in portions so that the temperature remained between 70 and 75° (a water bath was needed at times). After the addition (90 min), 500 ml of 30% H_2O_2 was added, and the red-brown liquid was stirred for 2 hr at 70 to 75°. The mixture was next poured into 40 liters of water and stirred for 1 hr. The solid was filtered and washed by stirring with 40 liters of water for 30 min. Crude product was dried overnight under vacuum; 192 g, 80% yield. The nmr spectrum showed an impurity of 10 to 12%. The recrystallization from dichloromethane/hexane gave 128.6 g of 100% pure product by gc analysis; yield, 53.7%.

3.7.5 Preparation of 4-Amino-3,5-Dinitrotoluene (IV) and 3,5-Dinitrotoluene (III)



3,5-Dinitro-N-Acetyl-p-Toluidine (XXIV)

In a three-neck flask equipped with a mechanical stirrer and thermometer was placed 2.45 liters of 90% HNO_3; this was cooled to 10° in an ice bath, and 198 g of N-acetyl p-toluidine was added over 50 min. With the temperature kept below 15°, the reactor was stirred for 25 min at about 15°. The solution was quenched into 2 x 4 liter Erlenmeyer flasks containing crushed ice and was stirred for 1 hr. The solid was filtered and washed by stirring with water in 3 x 4 liter Erlenmeyer flasks for 20 min. The moist, slightly greenish-yellow product was collected and dried overnight.

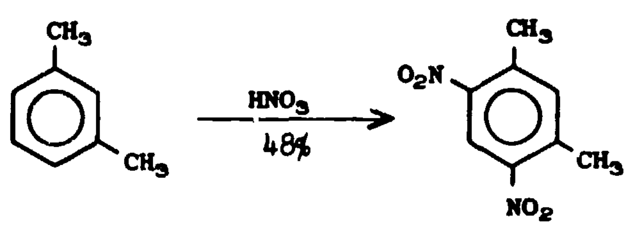
4-Amino-3,5-Dinitrotoluene (IV)

The product obtained from the preceding process was hydrolized by treatment with 1.2 liters of 50% H_2SO_4 at 90° for 30 min. The reaction mixture was cooled and filtered, and the product was washed thoroughly with water and dried under vacuum; 161.6 g, 61.7% yield.

3,5-Dinitrotoluene (XII)

4-Amino-3,5-dinitrotoluene (160 g) was mechanically stirred with 3.4 liters of abs. ethanol and 900 ml of conc. H_2SO_4 in a 12-liter three-neck flask; 544 g of $NaNO_2$ was added in portions (3 hr). When about 120 g of $NaNO_2$ had been added, the flask was heated to 70°. The reaction occurred vigorously, causing a strong evolution of gases, and the temperature rose to 78°. The flask was cooled to 60° in a water bath. During this time, a yellow solid appeared. The rest of the $NaNO_2$ was added to maintain the temperature at between 60 and 70°. The dense reaction mixture was then poured into 12 liters of water, stirred for 15 min, and filtered. The solid was washed with 8 liters of water, filtered, and dried for 36 hr under vacuum; wt, 129.7 g. Recrystallization from petroleum ether (60 to 110°) gave 96.8 g of 3,5-dinitrotoluene; yield, 65.6%.

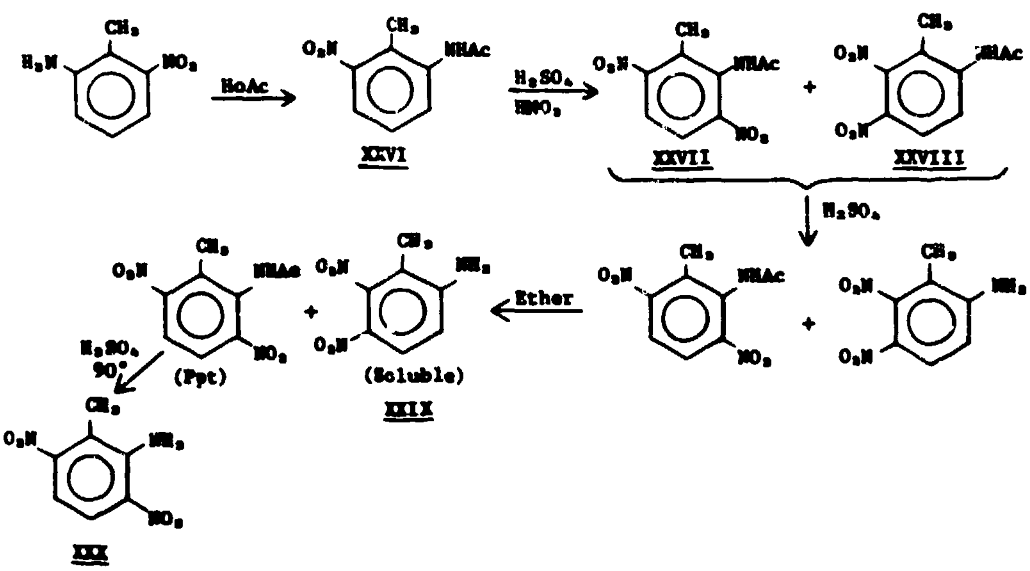
3.7.6 Preparation of 1,5-Dimethyl-2,4-Dinitrobenzene (XXV)



XXV

m-Xylene (100 g) was added slowly (over 15 min) to 280 ml of 90% HNO_3, with the temperature kept below 0°. The mixture was allowed to warm to room temperature. The heat of reaction allowed the reaction temperature to reach 90°, where it remained for about 1 hr; then heat was applied to keep the flask at 95° for 5 hr. The orange-red liquid was poured into 3 liters of ice/water, stirred 30 min, and filtered. This product was washed with water, 30 g $NaHCO_3$/500 ml H_2O, and again with water and dried overnight under vacuum; wt, 179.7 g. The gas chromatogram showed that the constituents of the product were 30% 1,3-dimethyl-2,4-dinitrobenzene and 70% 1,5-dimethyl-2,4-dinitrobenzene (column, 10 feet x 1/8 inch; 25% DOW 550 on 100/120 mesh Chromasorb). The recrystallization from 95% ethanol gave [illegible] g of greenish crystals of 98.5 to 99% 1,5-dimethyl-2,4-dinitrobenzene; mp, 91-93°; yield, 48%.

3.7.7 Preparation of 2-Amino-5,6-Dinitrotoluene (XXIX) and 2-Amino-3,6-Dinitrotoluene (XXX)



2-Methyl-3-Nitroacetanilide (XXVI)

2-Amino-6-nitrotoluene (50 g, 0.329 mol) was suspended in 400 ml of glacial acetic acid; the mixture was cooled to 5°, and 60 ml of acetic anhydride containing 0.5 g of 96% sulfuric acid was added in drops over 10 min. The temperature was raised to 85° over a 20-min period, during which time the desired product separated as a light-tan solid. After 10 min, the mixture was cooled to 40° and poured into 1 liter of crushed ice. The light-tan precipitate, 2-methyl-3-nitroacetanilide, was filtered, washed with water, and dried under vacuum; 61.0 g; 96% yield.

2-Methyl-3,6-Dinitroacetanilide (XXVII) and 2-Methyl-3,4-Dinitroacetanilide (XXVIII)

A nitrating solution was prepared by slowly adding 260 ml of 96% sulfuric acid to 152 ml of 90% nitric acid, keeping the temperature of the mixture below 25°. A 420-ml sample of this solution was cooled to 5°, and 60 g of 2-methyl-3-nitroacetanilide was added in small portions over 20 min while the temperature was maintained at 4-7°. After addition, the temperature was allowed to rise to 15°, at which point the reaction was quenched on 1500 ml of crushed ice. The cream-colored product was filtered, washed thoroughly with water, and dried under vacuum; 70.0 g; 95% yield. This product was a mixture of 2-methyl-3,6-dinitroacetanilide and 2-methyl-3,4-dinitroacetanilide.

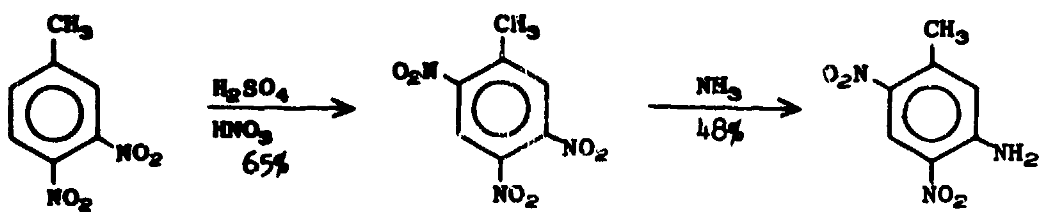
2-Amino-5,6-Dinitrotoluene (XXIX)

To a 69.0-g sample of a mixture of 2-methyl-3,6-dinitroacetanilide and 2-methyl-3,4-dinitroacetanilide was added 450 ml of 50% sulfuric acid. This stirred mixture was heated in a steam bath for 10 min to hydrolyze 2-methyl-3,4-dinitroacetanilide. The mixture was cooled to 40° and filtered, and the yellow product was dried under vacuum. This product was treated with 250 ml of ether to separate 2-amino-5,6-dinitrotoluene, which is soluble from 2-methyl-3,6-dinitroacetanilide. The filtrate was evaporated to dryness, leaving 2-amino-5,6-dinitrotoluene that was about 90% pure. Recrystallization from absolute ethanol yielded 19.4 g of pure product, which was identified by its nmr spectrum; 35% yield.

2-Amino-3,6-Dinitrotoluene (XXX)

The 2-methyl-3,6-dinitroacetanilide obtained from the preceding steps was placed in 300 ml of 50% sulfuric acid, and the stirred mixture was heated at 80 to 90° for 3 hr. The mixture was cooled and filtered, and the yellow product was dried under vacuum. Recrystallization from absolute ethanol gave 17.2 g of 2-amino-3,6-dinitrotoluene, which was identified by its nmr spectrum; 31% yield.

3.7.8 Preparation of 5-Amino-2,4-Dinitrotoluene (IX)



XXXI

IX

2,4,5-Trinitrotoluene (XXXI)

A mixture of 355 g of 3,4-dinitrotoluene, 3060 ml of 96% H_2SO_4, and 1150 ml of 90% HNO_3 was stirred and heated to 80 to 90° for 40 min. The mixture was poured into crushed ice and stirred for 20 min. The solid was filtered and washed by stirring with 30 liters of water during 1 hr. The crude product was dried under vacuum. The nmr spectrum showed about 25% impurity. After two crystallizations from 2 x 5 liters of abs. ethanol, 290 g of pure product with a consistent nmr spectrum was obtained; mp, 103 to 105°; 65.5% yield.

5-Amino-2,4-Dinitrotoluene (IX)

A mixture of 350 g of 2,4,5-trinitrotoluene and 3.5 liters of abs. ethanol was stirred at 60° until the solid was completely dissolved. The liquid was cooled to 15° in a dry ice/acetone bath, and 933 ml of 28% NH_4OH (d = 0.9) was added in portions (100 min) with stirring and at a temperature maintained at about 15°. The solution turned green and then dark blue after several portions of NH_4OH were introduced.

After the addition, the solution was refluxed for 1 hr and allowed to stand overnight. During that time, a brownish-black coarse solid was formed and deposited firmly onto the flask. The solid was filtered off and dried under vacuum to give a weight of 123 g.

The proton spectrum enabled us to identify it as the desired product, with 98.5 to 99% purity as shown by gc. The filtrate was condensed by distilling the solvent under the pressure of a water aspirator to 3 liters; this was left to stand over the weekend. An additional dark-yellow solid was collected (23%), and its nmr spectrum was identical to that of the first product.* Gc showed 88% purity; total crude product, 146 g; 48% yield. The purification by adding hexane to a hot solution of product in chloroform after the cooling gave a bright-yellow, fine powder that had a purity of 100% by gc analysis.

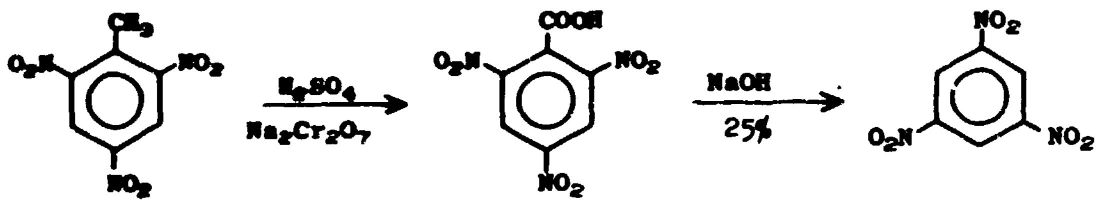
3.7.9 Alternative Method of Preparing 5-Amino-2,4-Dinitrotoluene

A mixture of 5.0 g of 2,4-dinitrotoluene (27.4 mmol) and 5.0 g of hydroxylamine hydrochloride (72.0 mmol) in 100 ml of abs. ethanol was cooled to 5°, and 50 ml of a solution of 85% KOH in methanol (saturated at ~5°) was added in drops (1 hr). The reaction mixture turned from white to blue-grey to red-brown as the KOH solution was added. Near the end of the addition, stirring was difficult because the KCl that precipitated had formed hard lumps. When the addition of the KOH was complete, the mixture was stirred at 10° for 30 min and 1500 ml of water was added, causing the KCl to dissolve and an organic product to precipitate. This product was collected by filtration, washed with water, and dried under vacuum over P_2O_5; wt, 3.77 g.

*The filtrate of the second crop was unintentionally left uncovered for several days. The solvent evaporated, leaving coarse yellow-brown needles that caused laboratory personnel to cough and sneeze. The compound was later purified by dissolution in water and extraction with chloroform and was identified as ammonium-3-methyl-2-6-dinitrophenolate by gc, nmr, and melting point methods.

An nmr spectrum showed that this product was approximately 75% 5-amino-2,4-dinitrotoluene and 25% 2,4-dinitrotoluene. For purification, the sample was treated with 50 ml of a mixture of 95% petroleum ether (60 to 110° and 5% toluene (hot) in which 2,4-dinitrotoluene was soluble. The insoluble material, 2.90 g, was analyzed by gc and found to be 84% 5-amino-2,4-dinitrotoluene. Further purification through recrystallization yielded a product that was [illegible] gc analysis; 40% yield.

3.7.10 Preparation of 1,3,5-Trinitrobenzene (XV)



XXXII XV

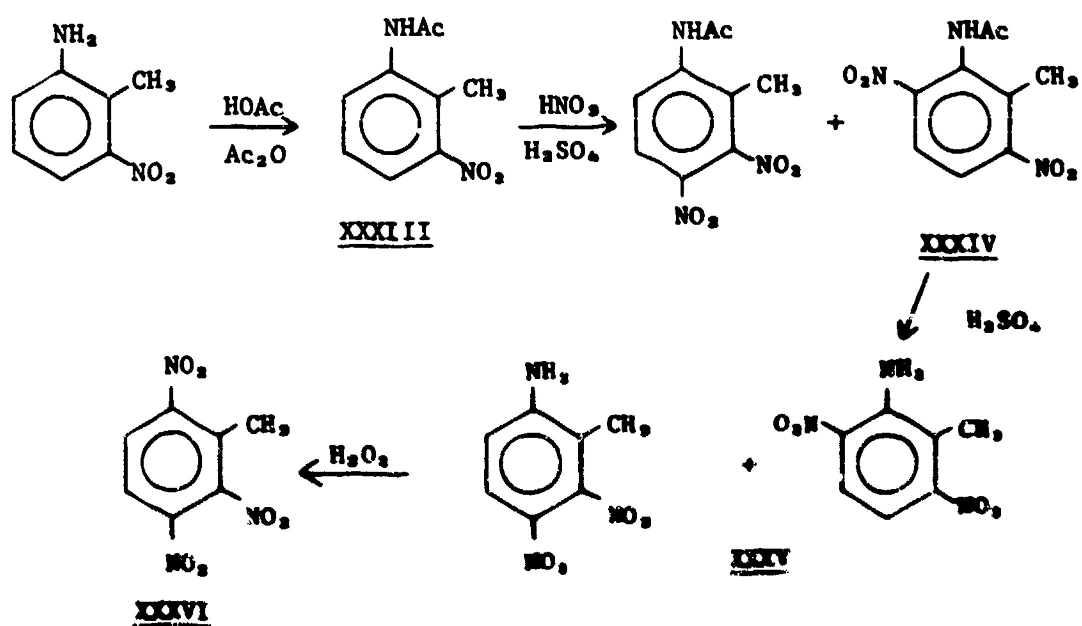
2,4,6-Trinitrobenzoic Acid (XXXII)

To 1500 cc of conc. sulfuric acid in a 5-liter flask was added 270 g (1.19 mol) of 2,4,6-trinitrotoluene during mechanical stirring. Sodium dichromate was then added in portions with continued stirring until the temperature reached 40°. A cold water bath was used to hold the temperature between 40 and 50° while sodium dichromate addition continued over a 2-hr period. A total of 406 g (1.36 mol) of sodium dichromate was added. When all the dichromate had been added, the mixture was stirred for 2 hr at 45 to 50° and then allowed to stand overnight. The mixture was carefully poured onto cracked ice, and the crude trinitrobenzoic acid was filtered through sintered glass and washed with cold water. After drying under vacuum, the product weighed 158 g (52% of the theoretical amount).

1,3,5-Trinitrobenzene (XV)

The crude trinitrobenzoic acid previously obtained was mixed with 1600 cc of water at 35° in a 5-liter flask. A 15% solution of sodium hydroxide was then added in portions with mechanical stirring, the temperature being held between 35 and 40°, until a yellow-red color appeared and trinitrobenzene floated on the surface. The solution was made just yellow with glacial acetic acid. The mixture was filtered, and the filtrate was transferred to a 5-liter flask; 50 cc of glacial acetic acid was added, and the solution was heated gently with mechanical stirring for 3.5 hr. The mixture was allowed to stand for 48 hr and then was filtered to yield 62.8 g (25% of the theoretical amount from trinitrotoluene) of pure 1,3,5-trinitrobenzene.

3.7.11 Preparation of 2,3,6-Trinitrotoluene (XXXVI)



2-Methyl-3-Nitroacetanilide (XXXIII)

2-Methyl-3-nitroaniline (200 g, Aldrich) was suspended in 1600 ml of glacial acetic acid. The mixture was cooled to 5°, and 240 ml of acetic anhydride containing 0.5 g of 96% sulfuric acid was added in drops over 15 min. The temperature was raised to 85° over 25 min, during which time the desired product separated as a light-brown solid. After the reaction temperature had been held at 85° for 10 min, the mixture was cooled to 40° and poured into 4 liters of crushed ice. The light-brown precipitate was filtered, washed with water, and dried under vacuum; 92.5% yield.

2-Methyl-3,5-Dinitroacetanilide and 2-Methyl-3,[illegible]-Dinitroacetanilide (XXXIV)

A mixed acid solution was prepared by slowly adding 1034 ml of 96% sulfuric acid to 646 ml of 90% nitric acid, keeping the temperature of the mixture below 25°. A 1680-ml sample of mixed acid was cooled to 5°, and 240 g of 2-methyl-3-nitroacetanilide was added in small portions ([illegible] min) while the temperature was maintained at 4 to 7°. After addition, the temperature was allowed to rise to 15°, at which point the reaction was quenched on 6 liters of crushed ice. The cream-colored precipitate was filtered, washed thoroughly with water, and dried [illegible]; [illegible].1 g; 97% yield.

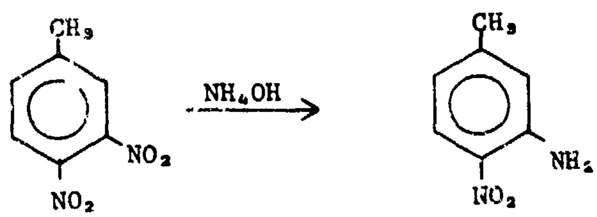
2,4-Dinitro-6-Aminotoluene and 3,6-Dinitro-2-Aminotoluene (XXXV)

To a 206-gram sample of the mixed dinitroacetanilides (0.87 mol) was added 1340 ml of 50% sulfuric acid with stirring. The mixture was heated on a steam bath at 80 to 90° for 2 hr, during which time a yellow-orange solid formed. The hot mixture was quenched on 8 liters of crushed ice and allowed to stand overnight. The solid was filtered, washed thoroughly with water to remove all traces of acid, and vacuum dried over sulfuric acid; 159.6 g; 93% yield.

2,3,6-Trinitrotoluene (XXXVI)

Trifluoroacetic anhydride (570 ml) was added quickly (5 min) to 835 ml of $CHCl_3$, with the temperature held at about 5°. A 90-ml sample of 90% hydrogen peroxide was added in drops (2 hr), with the temperature maintained between 0 and 5°. To this milky white mixture was added the above aminodinitrotoluenes (159.6 g) in small portions (30 min) at 0 to 5°. The reaction temperature was allowed to rise slowly to 54° (40 min), the dropping funnel was replaced by a condenser, and the mixture was refluxed for 2 hr. The reaction was cooled to ambient temperature, and solvents were removed on a rotary evaporator until a yellow precipitate appeared. Methylene chloride was added to dissolve the precipitate, and the resulting solution was washed with four 250-ml portions of 5% $NaHCO_3$ and two 250-ml portions of water. The methylene chloride solution was dried ($MgSO_4$), the solvent was removed under vacuum, and the yellow crystalline product was dried under vacuum. The product (180.? g) represented a yield of 91%; mp 105 to 112°; purity, 99% by gc analysis. Recrystallization from 1250 ml of methanol gave 124.3 g of pure 2,3,6-trinitrotoluene; mp, 111.5 to 112.5°.

3.7.12 Preparation of 3-Amino-4-Nitrotoluene (XXXVII)



XXXVII

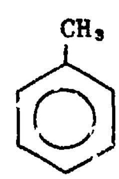
A 115-g sample of 3,4-dinitrotoluene, 284 ml of ammonium hydroxide solution (28% NH_3), and 1750 ml of methanol were heated in an autoclave for 6 hr at 150°. After the methanol was evaporated under vacuum the yellow-brown residue was crystallized twice from methanol to yield 58.4 g of pure 3-amino-4-nitrotoluene; yield, 61%.

4 ANALYTICAL CHEMISTRY EVALUATIONS OF MUNITIONS COMPOUNDS USED IN TOXICOLOGICAL EVALUATIONS

The compounds used in aquatic and mammalian toxicological studies were evaluated for their identity and purity. For identification, infrared (ir), nuclear magnetic resonance (proton nmr), ultraviolet spectroscopy (uv), and mass spectral data were obtained. For purity, each compound was evaluated for its elemental composition and chromatographic homogeneity using gc and hplc. The results for each compound and the spectral and chromatographic data are presented in the following sections. Uv spectra were taken on a Perkin-Elmer Model 200 uv spectrophotometer; ir spectra were obtained from a Perkin-Elmer 137 infrared spectrophotometer; nmr spectra were obtained on Varian A-60A or Varian EM-90 nuclear magnetic resonance spectrometers; and mass spectra were obtained on a LKB 9000 mass spectrometer.

4.1 Toluene

Methyl benzene
[108-88-3]



Source: Mallinckrodt
Lot BPB
Catalog No. 8608

Identity

IR—The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference No. 419 for toluene. The following bands were observed: (neat) 3.35 (=C-H, aromatic), 3.5 (C-H, methyl), 5-6 (aromatic overtones, mono-substituted benzene), 6.2, 6.85 (C-C, ring), 9.7, 13.7 (C-H), 7.3, 8.5, 9.25, 11.J um.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals: δ 2.32 (singlet, CH_3); δ 7.17 (singlet, H_a).

uv (Methanol)--λ_{max} = 209.0 nm, A = 0.397, ε = 6590
λ_{max} = 263.0 nm, A = 0.016, ε = 256.

Purity (>95%)

Elemental Analysis--

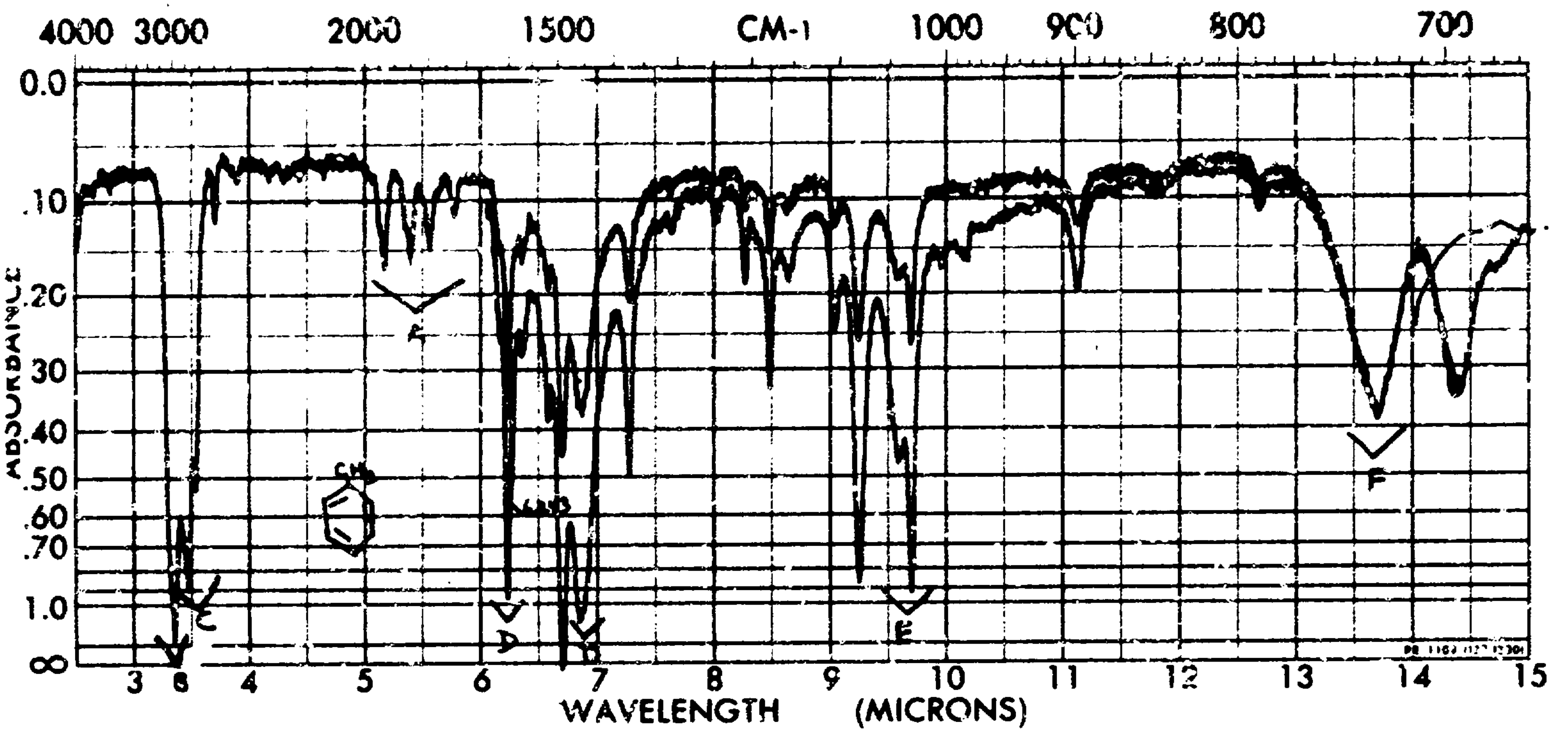
Anal. for C_7H_8: Calcd: C, 91.25; H, 8.75
Found: C, 91.30; H, 8.64.

High-Pressure Liquid Chromatography--One peak was observed representing 100% of total peak area. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow Rate: 1.0 ml/min
- Detection: uv at 254 nm
- Average retention time: 773 sec toluene 100%.

Gas Chromatography--One major component (representing 95.4% of total peak areas) and at least six minor components were observed by gc under the following conditions:

- Column: 5' x 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 110 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 66 sec toluene 89.4%.



SPECTRUM NO. 18	ORIGIN	LEGEND A: OVERTONES mono-substituted benzene	REMARKS
SAMPLE TOLUENE (NEAT)		1. B: C-H stretch-aromatic. C: C-H stretch - methyl	E: In plane C-H bend
	PURITY	2. D: C=C ring stretch	F: Out of plane C-H stretch.
MALLINCKRODT LOT BPB	PHASE	DATE MAY 23, 1977	
	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO. 41
SAMPLE

RECORDING CHARTS

FIGURE 7 INFRARED SPECTRUM OF TOLUENE

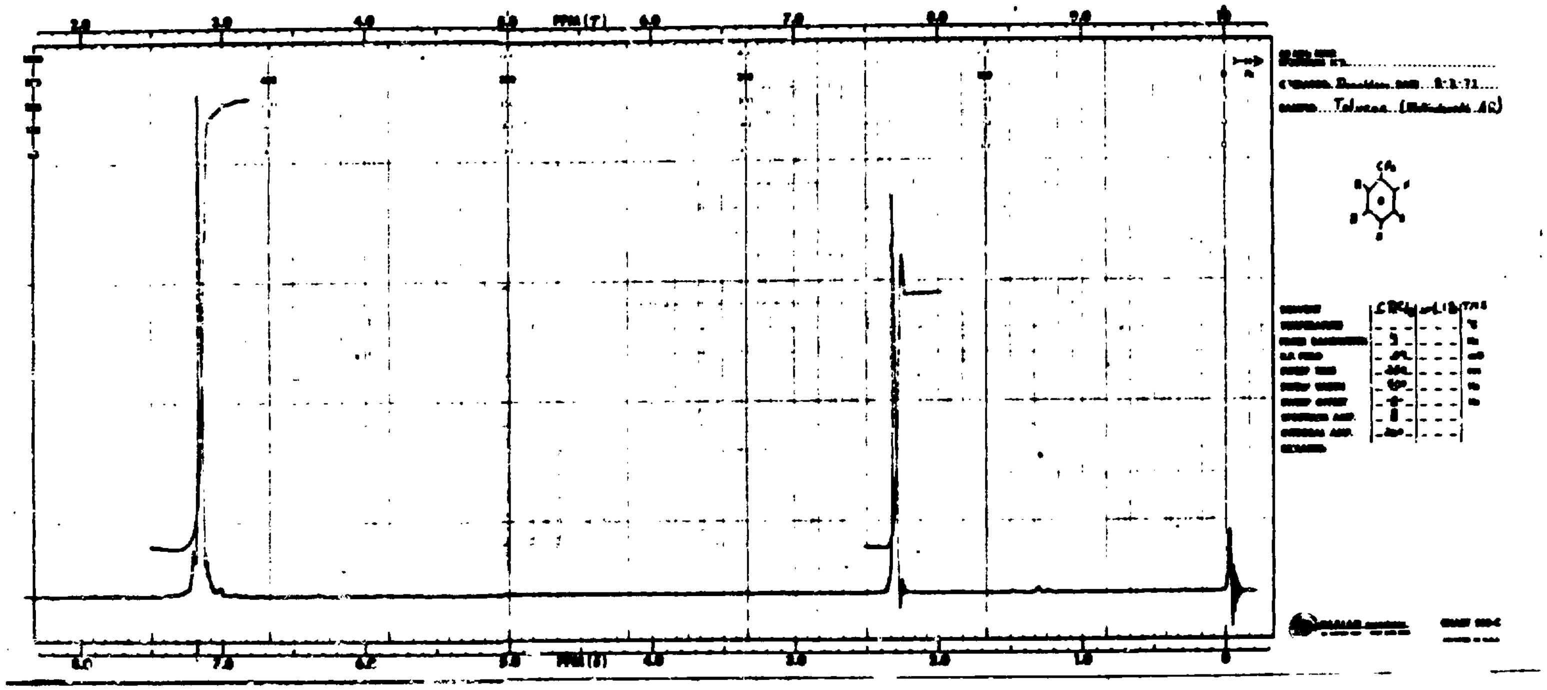
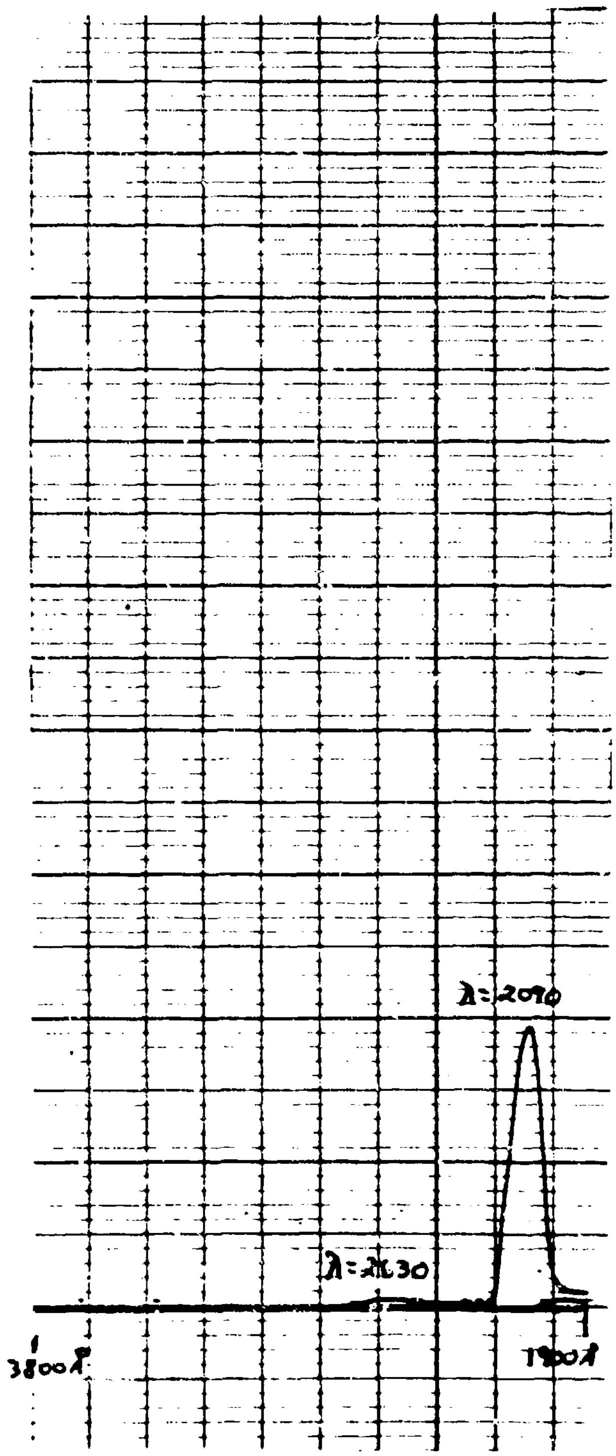


FIGURE 6 NMR SPECTRUM OF TOLUENE



Toluene

$C = 6.02 \times 10^{-5}$ M/l

$A_{2090Å} = .397$
$\epsilon_{2090Å} = 6590$

$A_{2630Å} = .016$
$\epsilon_{2630Å} = 256$

FIGURE 9 UV SPECTRUM OF TOLUENE

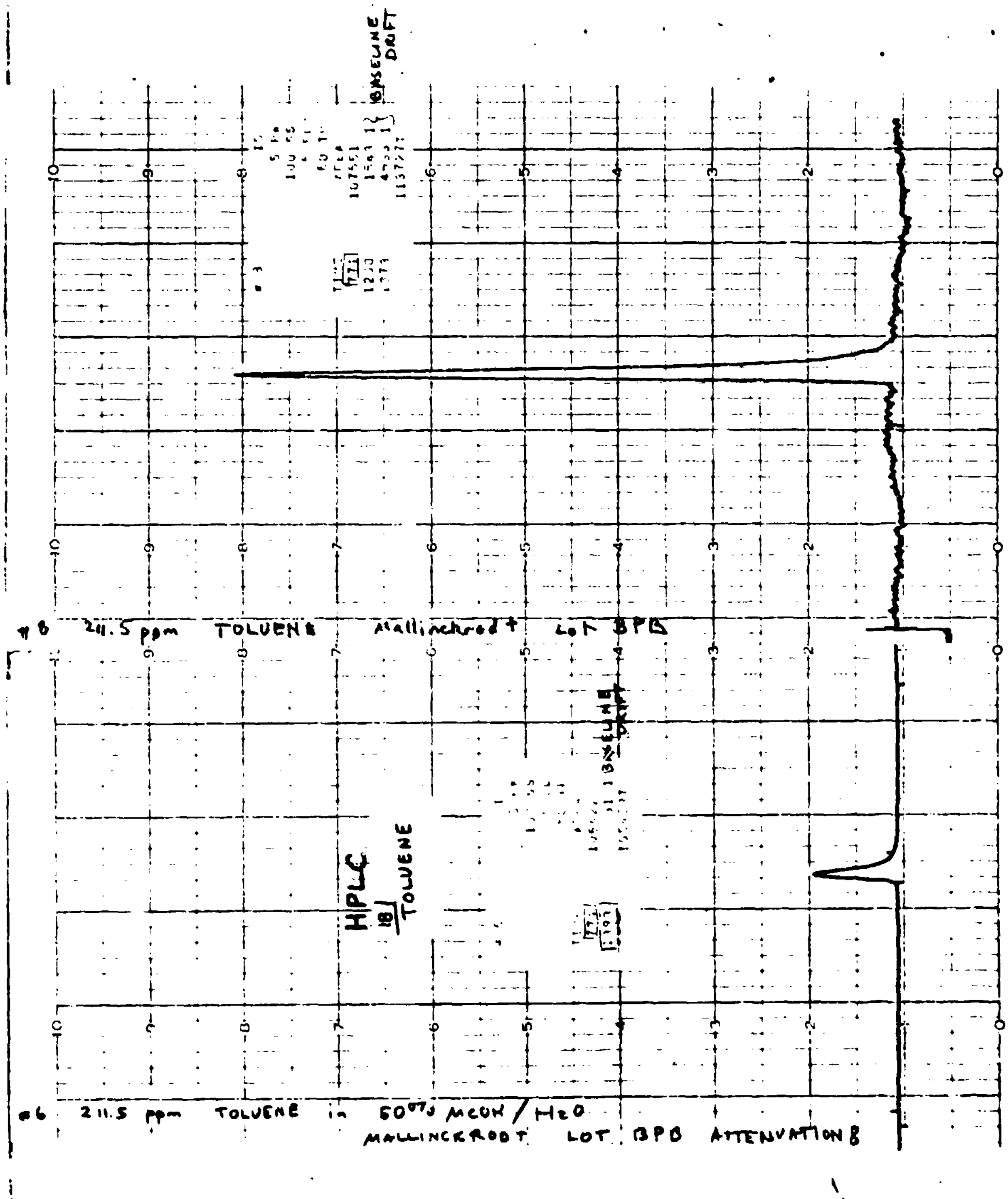


FIGURE 10 HPLC CHROMATOGRAM OF TOLUENE

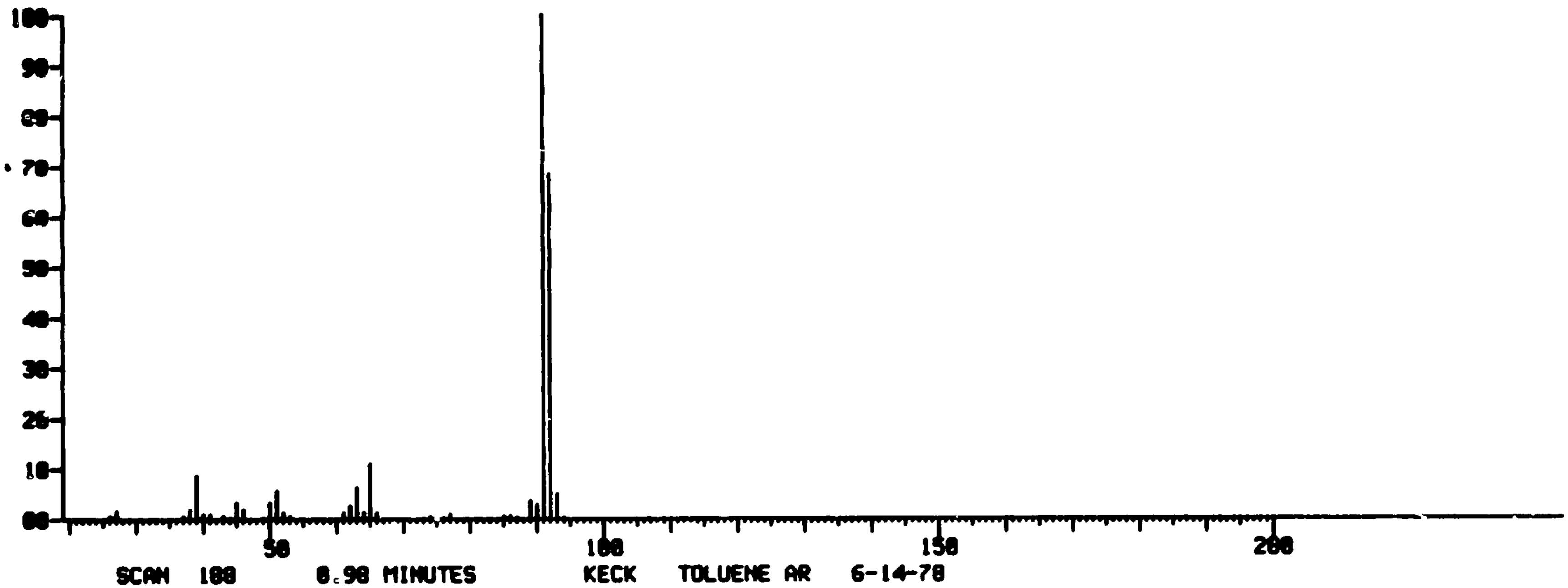


FIGURE 11 MASS SPECTRUM OF TOLUENE

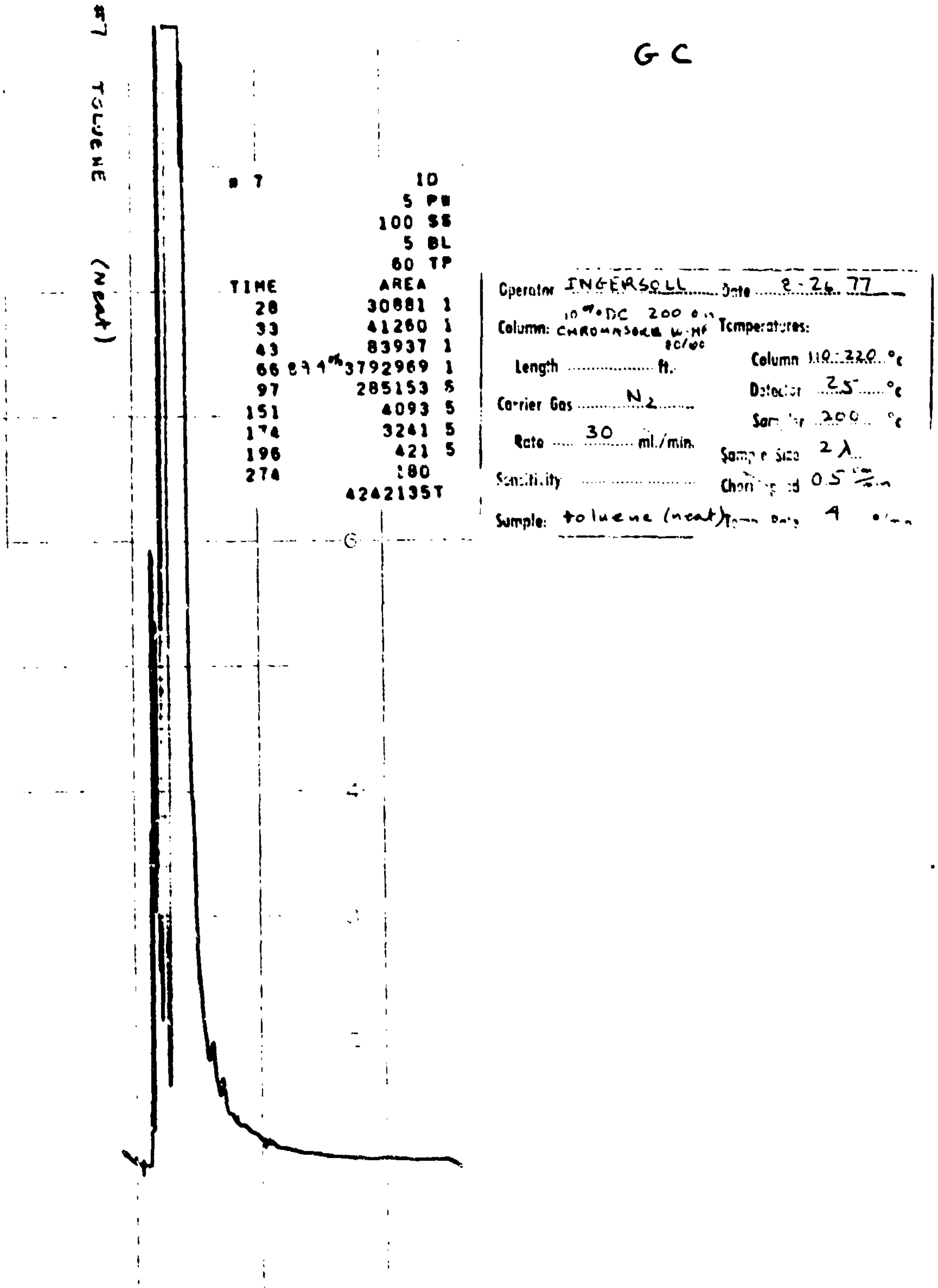
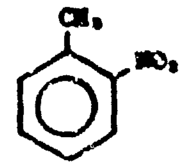


FIGURE 12 GC SPECTRUM OF TOLUENE

4.2 <u>2-Nitrotoluene</u>

1-Methyl-2-nitrobenzene

[88-72-2]



Source: **Eastman Organic Chemicals**
No lot listed
Catalog No. 193

<u>Identity</u>

<u>Ir</u>--The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference No. 4692 for 2-nitrotoluene. The following bands were observed: (neat) 3.3 (=C-H, aromatic), 3.4 (C-H, methyl), 5-6 (aromatic overtones, ortho-benzenoid substitution), 6.2, 6.8 (C=C, ring), 6.5 7.4 (N=O), 9.5, 9.6 (C-H), 11.6 (C-N, aromatic NO_2), 8.3, 8.6, 8.7, 9.2, 10.4, 12.2, 14.5 µm.

<u>Nmr</u>--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

($CDCl_3$): δ 2.60 (singlet, 3H) CH_3; δ 7.40 (multiplet, 3H) H_a;
δ 7.93 (multiplet, H) H_b, J_{a-b} = 8 cps), J_{b-a} = 7.5, $J_{b-a'}$ = 3).

<u>uv (Methanol)</u>--λ_{max} = 207.2 nm, A = 0.590, ϵ = 10,900
λ_{max} = 257.0 nm, A = 0.295, ϵ = 5440.

<u>Purity</u> (99.5% ± 0.5)

<u>Elemental Analysis</u>--

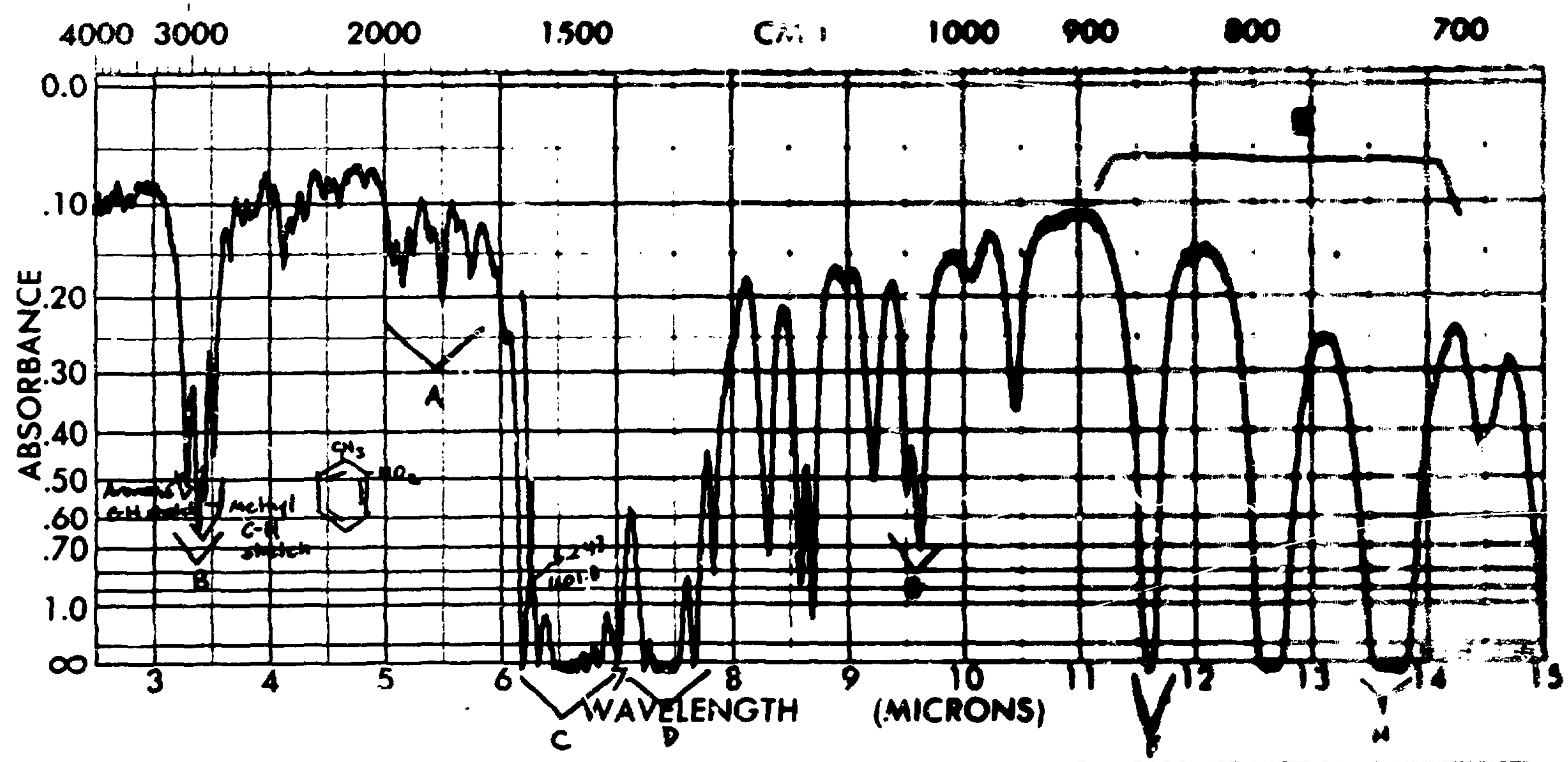
Anal. for $C_7H_7NO_2$: Calcd: C, 61.3; H, 5.1; N, 10.2
Found: C, 61.02; H, 4.98; N, 10.24.

High-Pressure Liquid Chromatography--One peak representing 100% of total peak areas was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 827 sec 2-nitrotoluene 100%.

Gas Chromatography--One major component (representing 99.0% of total peak areas) and two minor components were observed by gc under the following conditions:

- Column: 5' x 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 412 sec 2-nitrotoluene 99.0%; [illegible] sec impurity 0.5%; 519 sec impurity 0.5%.



SPECTRUM NO. 1	ORIGIN	LEGEND A: ortho-benzenoid substitution	REMARKS
SAMPLE o-NITROTOLUENE (Neat)		1. B: Aromatic C-H { Methyl C-H C: C=C ring stretch { N=O asymmetric	E: Interaction of NO₂ { C-H bending F Aromatic NO₂ C-N stretch
	PURITY	2. D: N=O symmetric	G In Plane C-H bend
EASTMAN LOT #193	PHASE	DATE MAY 23, 1977	H: Out of plane C-H bend
SADTLER 4692	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO
SAMPLE

FIGURE 13 INFRARED SPECTRUM OF 2-NITROTOLUENE

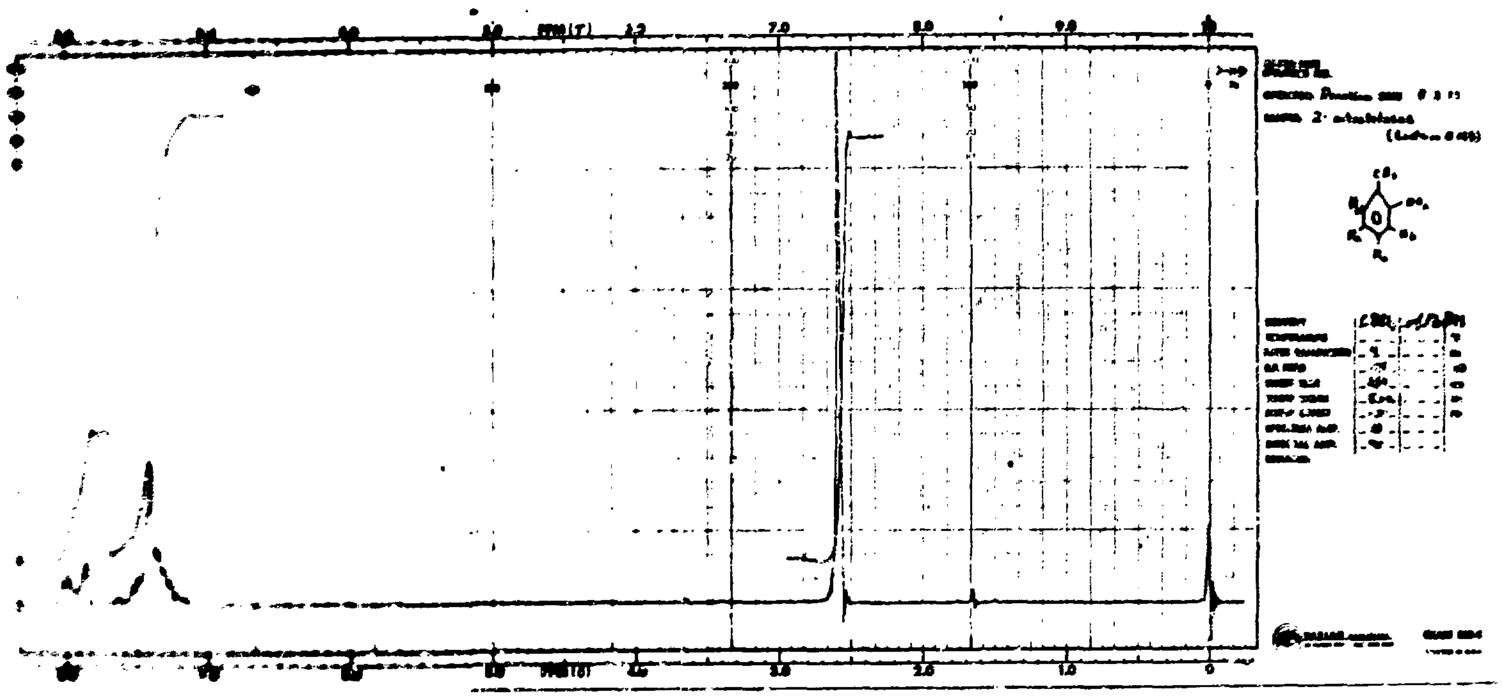
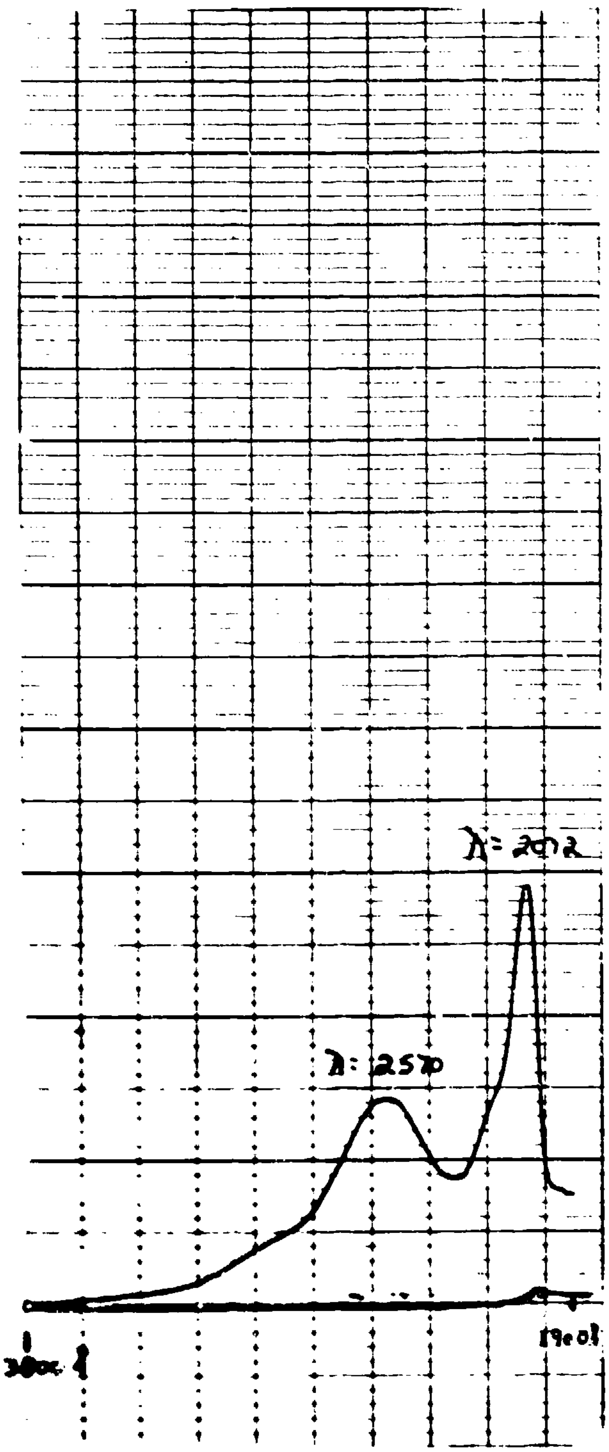


FIGURE 14 NMR SPECTRUM OF 2-NITROTOLUENE



2-nitrotoluene

$C = 5.42 \times 10^{-5}\ M/l$

$A_{2072Å} = .590$
$\epsilon_{2072Å} = 10900$

$A_{2570Å} = .295$
$\epsilon_{2570Å} = 5440$

FIGURE 15 UV SPECTRUM OF 2-NITROTOLUENE

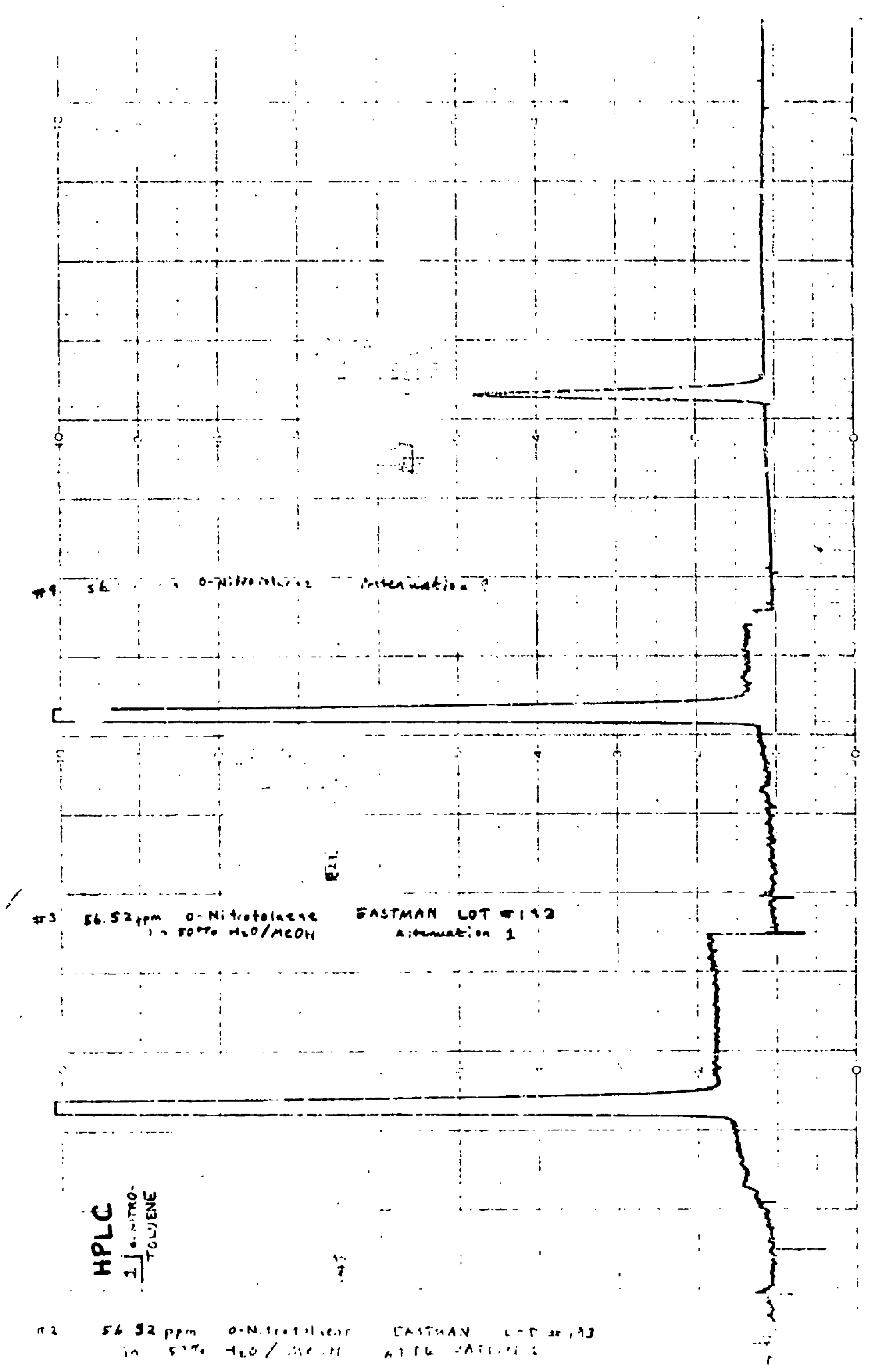
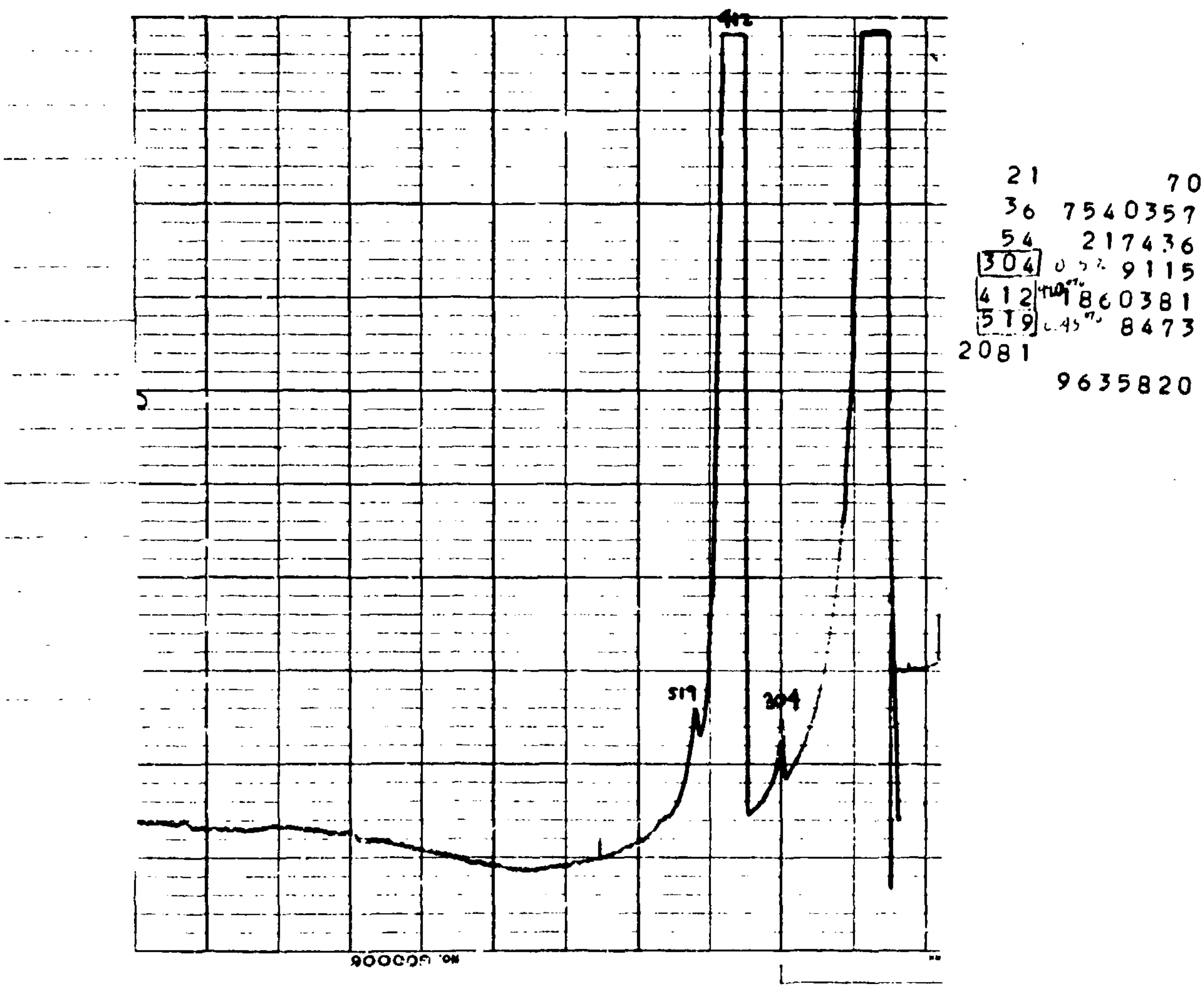


FIGURE 16 HPLC CHROMATOGRAM OF 2-NITROTOLUENE

GC

Ortho - Nitrotoluene



Operator Donaldson Date 3-23-77

Column: [redacted] Temperatures:

DC 200

Length 5

Column 100-225°C

Carrier Gas N_2

Inj. 220 °C

Det. 200 °C

Flow 20

Sample size 2µl

Sensitivity 10^{-10}, Att 1

Chart speed .166 in/min

Sample: O-NT Temp. Rate 4 °/min.

FIGURE 17 GC SPECTRUM OF O-NITROTOLUENE

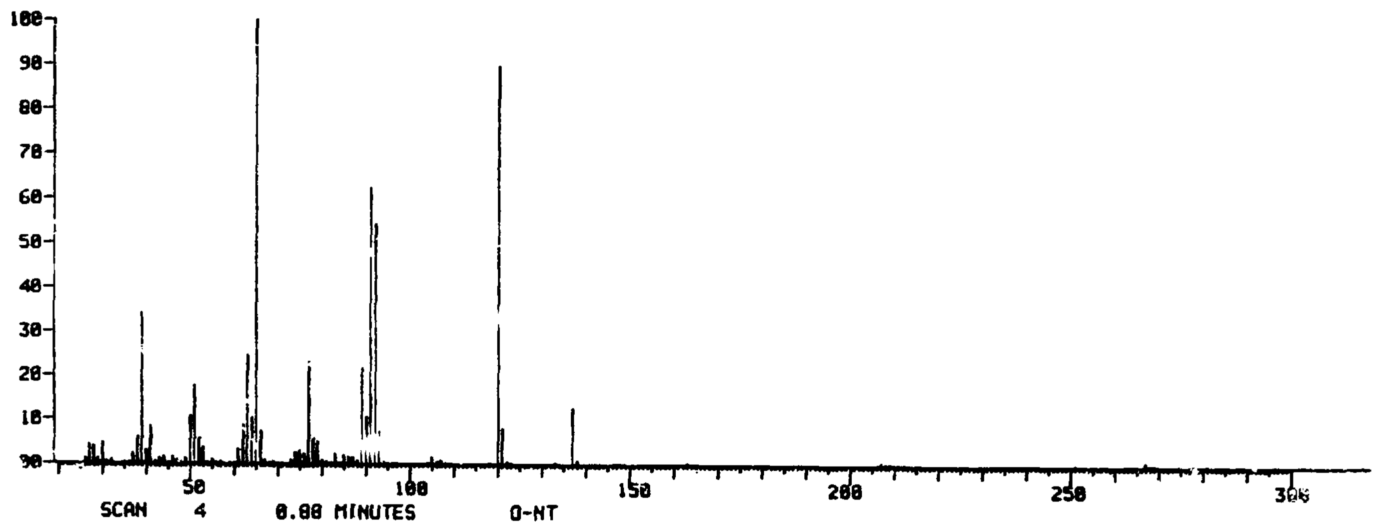
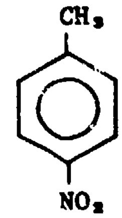


FIGURE 18 MASS SPECTRUM OF 2-NITROTOLUENE

4.3 **4-Nitrotoluene**
1-Methyl-4-nitrobenzene
[99-99-0]



Source: **Matheson Company**
Lot No. 303117
Catalog No. 2799

Identity

Ir--The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference No. 4693 for p-nitrotoluene. The following bands were observed: (thin film in $CHCl_3$) 3.4 (=C-H, aromatic), 3.5 (C-H, methyl), 5-6 (aromatic overtones, para-benzenoid substitution), 6.2, 6.8 (C=C, ring), 6.5, 7.4 (N=O), 9.6, 9.8 (C-H), 11.6 (C≡N, aromatic NO_2), 4.1, 8.3, 8.5, 9.05, 10.5, 14.7 µm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals: ($CDCl_3$); δ 2.43 (singlet, CH_3); δ 7.29 (doublet, H_a, J_{a-b} = 8 cps); δ 8.06 (doublet, H_b, J_{a-b} = 8 cps).

uv (Methanol)--λ_{max} = 260.0 nm, A = 1.392, ε = 8490
λ_{max} = 215.6 nm, A = 1.255, ε = 7650
λ_{max} = 273.2 nm, A = 1.551, ε = 9460.

Purity (100%)

Elemental Analysis--

Anal. for $C_7H_7NO_2$: Calcd: C, 61.3; H, 5.1; N, 10.2
Found: C, 60.97; H, 5.06; N, 10.24.

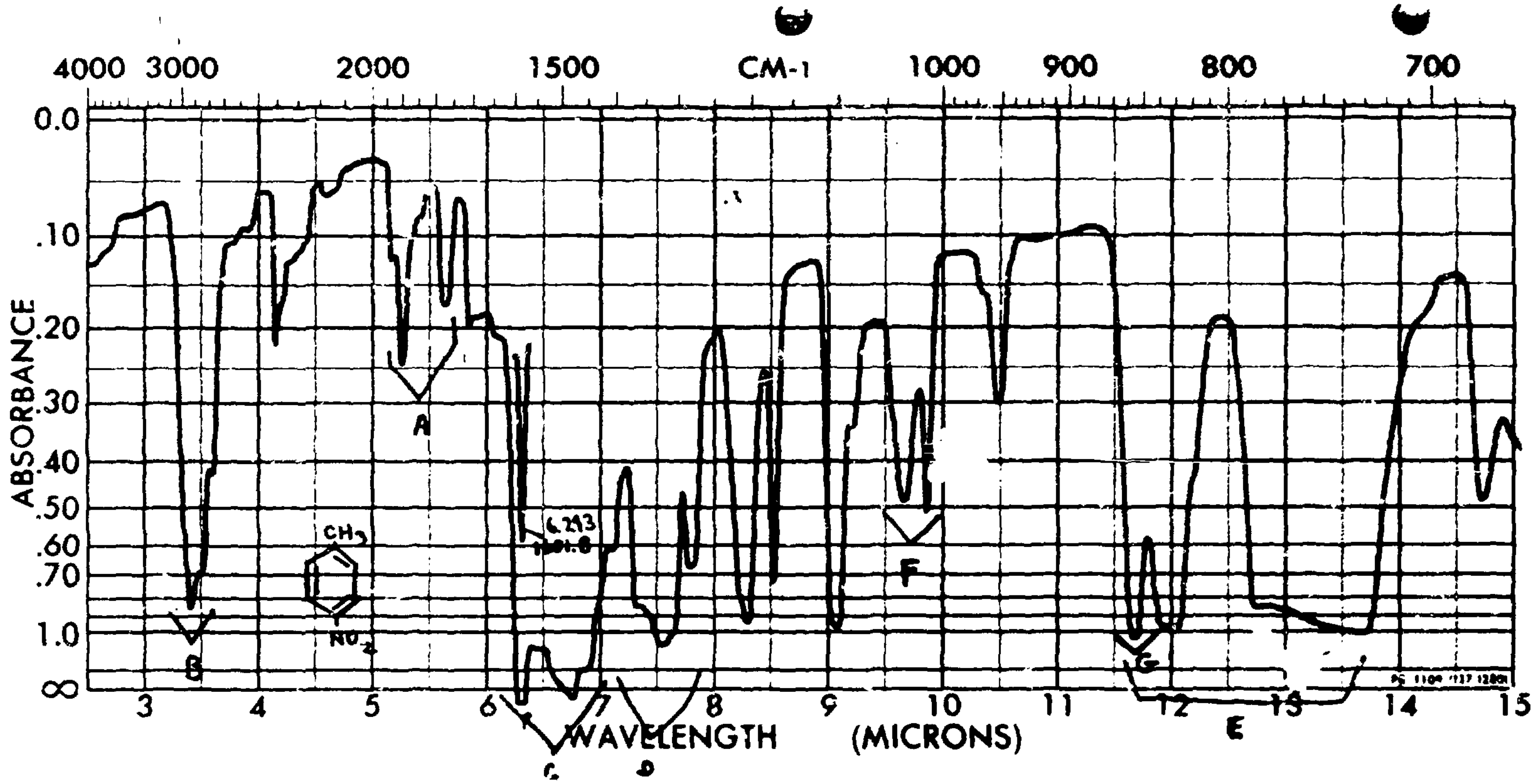
High-Pressure Liquid Chromatography--One peak (representing 100% of total peak areas) was obtained by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Retention time: 860 sec 4-nitrotoluene 100%

Gas Chromatography-- One peak (representing 100% of total peak areas) was observed by gc under the following conditions:

- Column: 5' x 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 33 sec 4-nitrotoluene 100%.

SPECTRUM NO. 3
SAMPLE



SPECTRUM NO. 2	ORIGIN	LEGEND	REMARKS
SAMPLE p-NITROTOLUENE in CHLOROFORM	NO REFERENCE CELL	1.	A: Overtone p-substituted
	PURITY	2.	B: C-H of $CHCl_3$ + aromatic
Matheson, Coleman & Bell 303117	PHASE	DATE APRIL 1977	C: C=C ring stretch + N=O stretch Asymmetric
SADTLER 4693	THICKNESS	OPERATOR C. Ingersoll	D: N=O symmetric E: interaction of NO_2 + CH bending F. F: In plane C-H bend. G: Ar-NO_2 C-N stretch.

FIGURE 19 INFRARED SPECTRUM OF 4-NITROTOLUENE

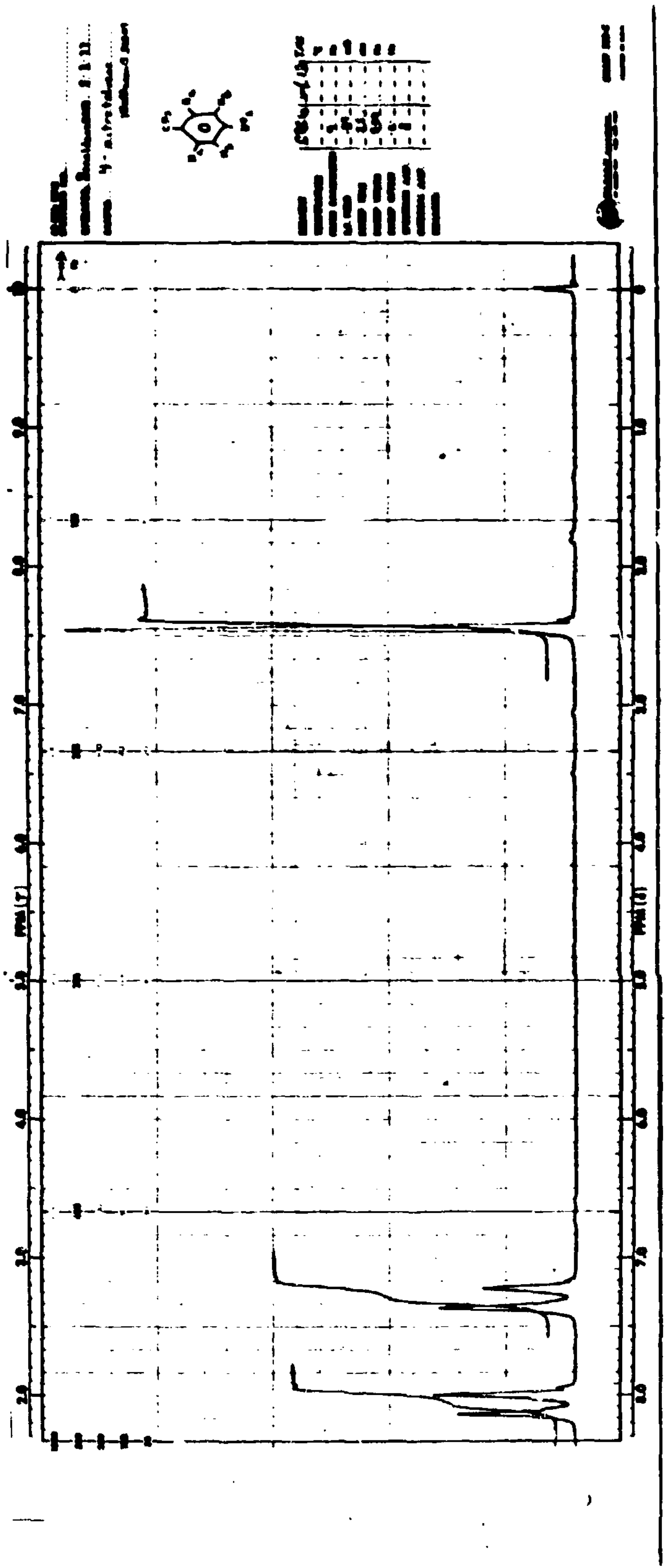


FIGURE 20 NMR SPECTRUM OF 4-NITROTOLUENE

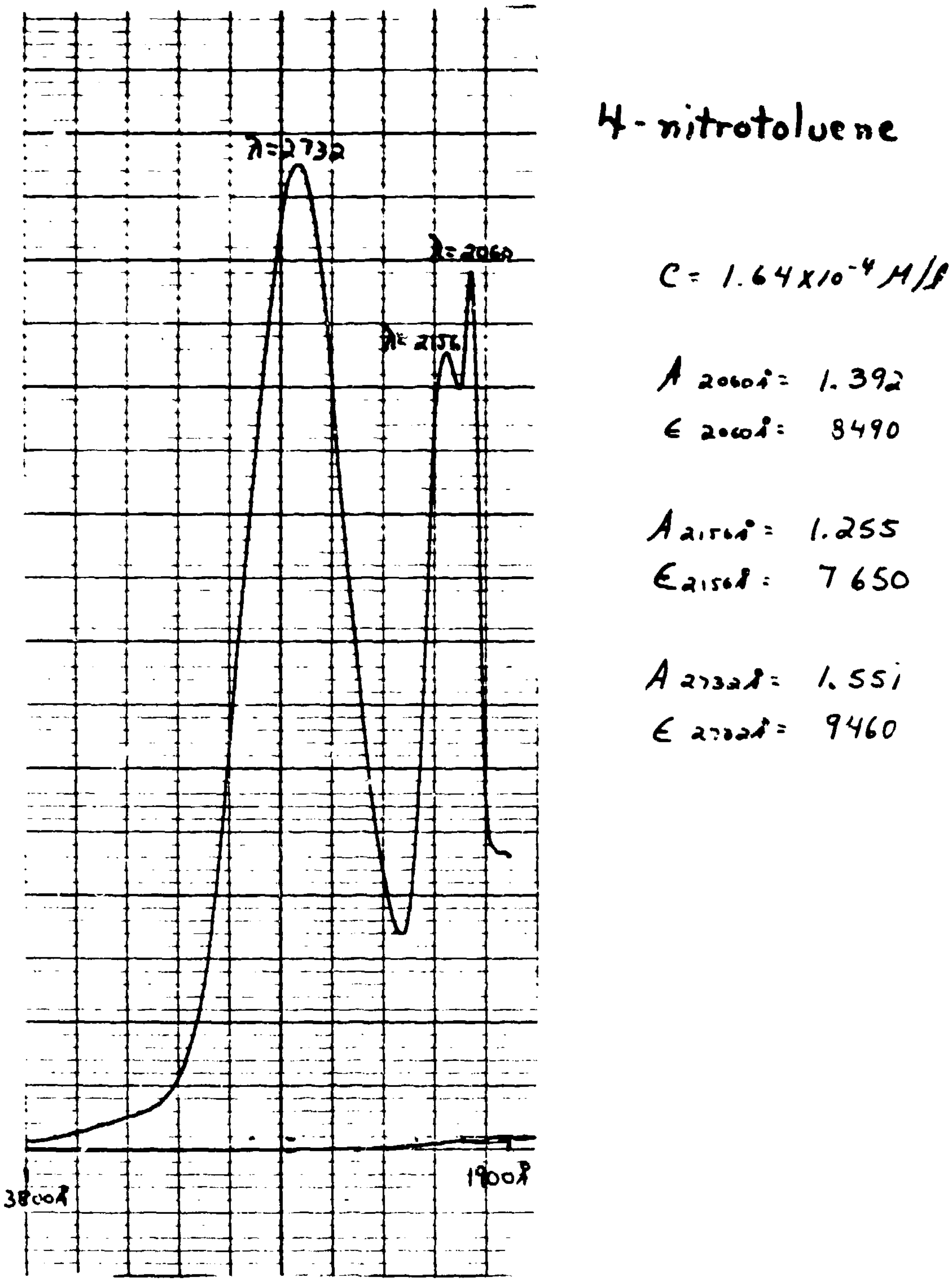


FIGURE 21 UV SPECTRUM OF 4-NITROTOLUENE

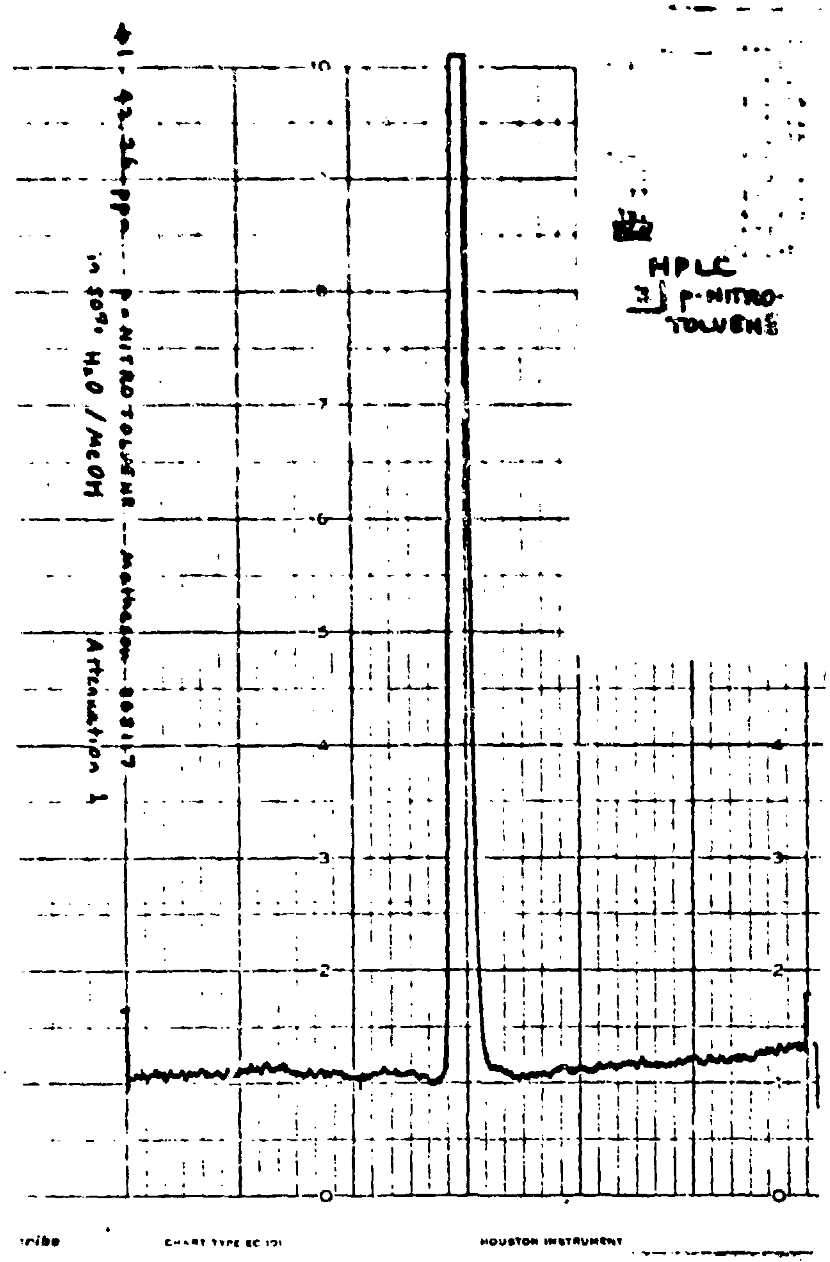
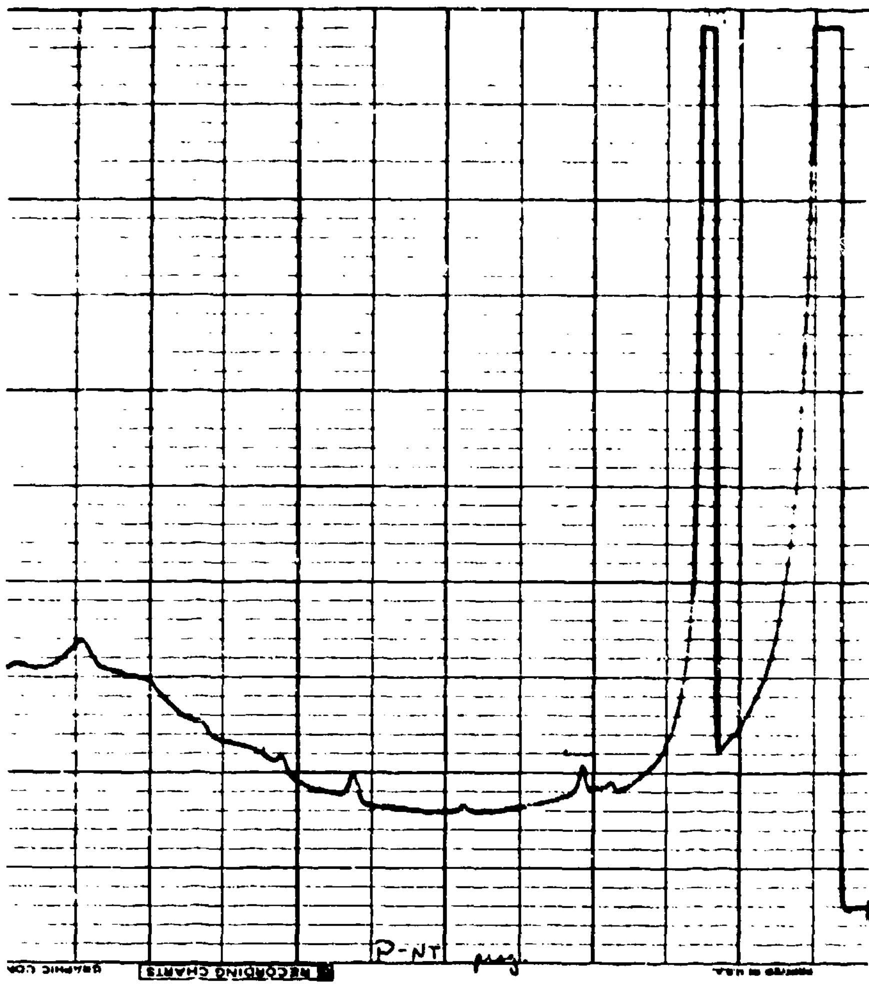


FIGURE 22 HPLC CHROMATOGRAM OF 4-NITROTOLUENE

para-Nitrotoluene



14	205
22	6594530
339	630607
653	687
1211	577
2754	
2873	19
	9226990

Operator: Donaldson Date: 3-23-77
10% DC 200 ... HP 80/100
Column: [redacted] Temperatures:
Length: 5 ft. Col.: 100-220°c
Carrier Gas: N_2 Det.: 220°c FID
Rate: 20 ml/min Inj.: 200°c
Sensitivity: 10^{-10} Sample: 2 μl
Chart: .16 in/min
Sample: P-NT 4

FIGURE 23 GC SPECTRUM OF 4-NITROTOLUENE

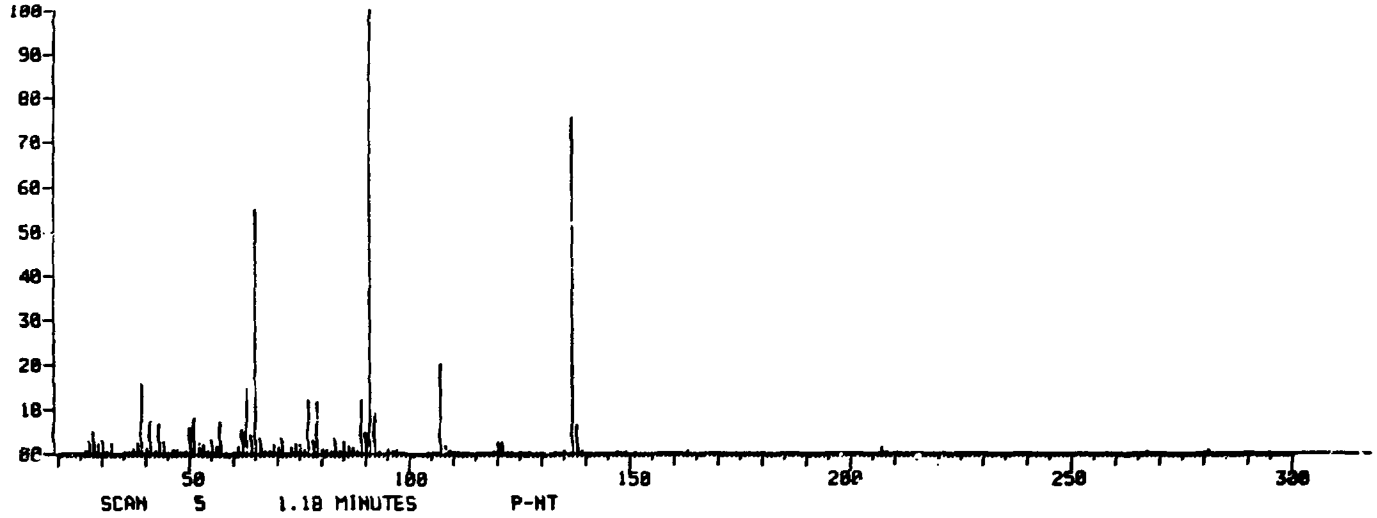
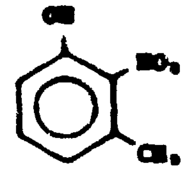


FIGURE 24 MASS SPECTRUM OF 4-NITROTOLUENE

4.4 3-Methyl-2-Nitrophenol [4920-77-8]



Source: Aldrich Chemical Company
Lot No. CZ1434
Catalog No. 16,074-1

Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 3.0 broad (intermolecular hydrogen-bonded O-H), 3.45 (C-H), 6.3, 6.9 (C=C, ring), 6.6, 7.5 (N=O), [illegible].4 (O-H), 8.4 (C-O), 9.4, 9.7 (C-H), 11.7 (C-N, aromatic NO_2), 10.4, 12.[illegible], 13.15 μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integral:

($CDCl_3$): δ 6.84 (doublet of multiplet, 1H, J_{a-b} = 7 cps) H_a
δ 7.00 (doublet of multiplet, 1H, J_{c-b} = 7 cps) H_c
δ 7.31 (doublet, 0.5H, J_{b-a} = 7 cps) H_b
δ 7.45 (doublet, 0.5H, J_{b-c} = 7 cps) H_b.

uv (Methanol)--λ_{max} = 213.6 nm, A = 1.118, ε = 9240
λ_{max} = 271.0 nm, A = 0.198, ε = 1640.

Purity (98.9% ± 1.1)

Elemental Analysis--

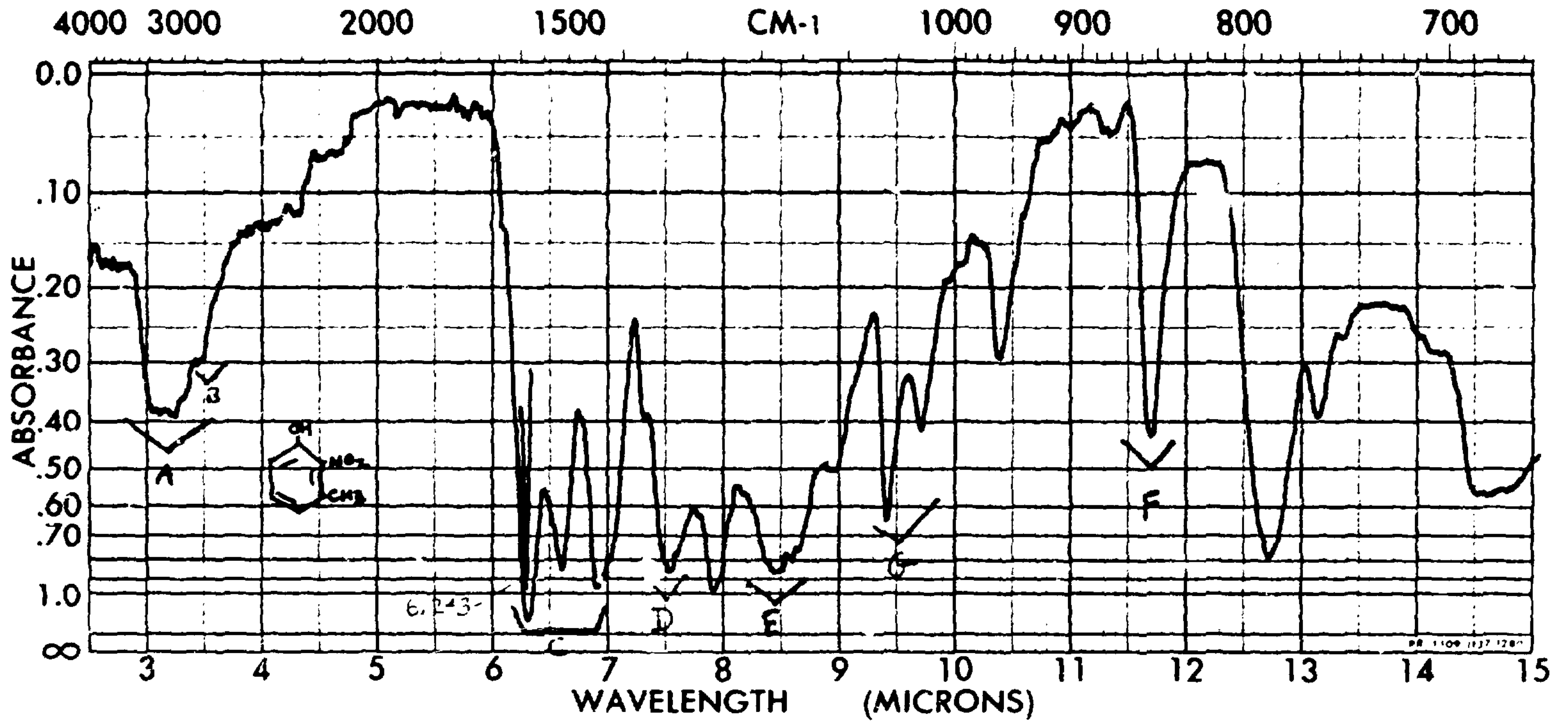
Anal. for $C_7H_7NO_3$: Calcd: C, 54.9; H, 4.61; N, 9.15
Found: C, 54.60; H, 4.5[illegible]; N, 9.15.

High-Pressure Liquid Chromatography--One major component (representing 97.8% of total integrated peak areas) and two minor components were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 307 sec 3-methyl-2-nitrophenol 97.8%; 81 sec impurities 2.2% (two peaks not separated).

Gas Chromatography--One major peak (representing 100% of total peak areas) was observed by gc under the following conditions:

- Column: 5' x 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 95 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 568 sec 3-methyl-2-nitrophenol 100%.



SPECTRUM NO.	ORIGIN	LEGEND A: Broad, intermolecular hydrogen bonded O-H stretch	REMARKS
SAMPLE 3-METHYL-2-NITROPHENOL		1. B: C-H stretch	
KBr PELLET	PURITY	C: C=C ring stretch (6.3, 6.9)	
		2. D: In plane O-H bend	§ N=O stretch
		E: C-O stretch	F: C-N stretch (aromatic NO2)
Aldrich	PHASE	DATE AUGUST 22, 1977	
LOT NO. 011454	THICKNESS	OPERATOR C. INGERSOLL	G: In plane C-H bend

SPECTRUM NO.
SAMPLE

FIGURE 25 INFRARED SPECTRUM OF 3-METHYL-2-NITROPHENOL

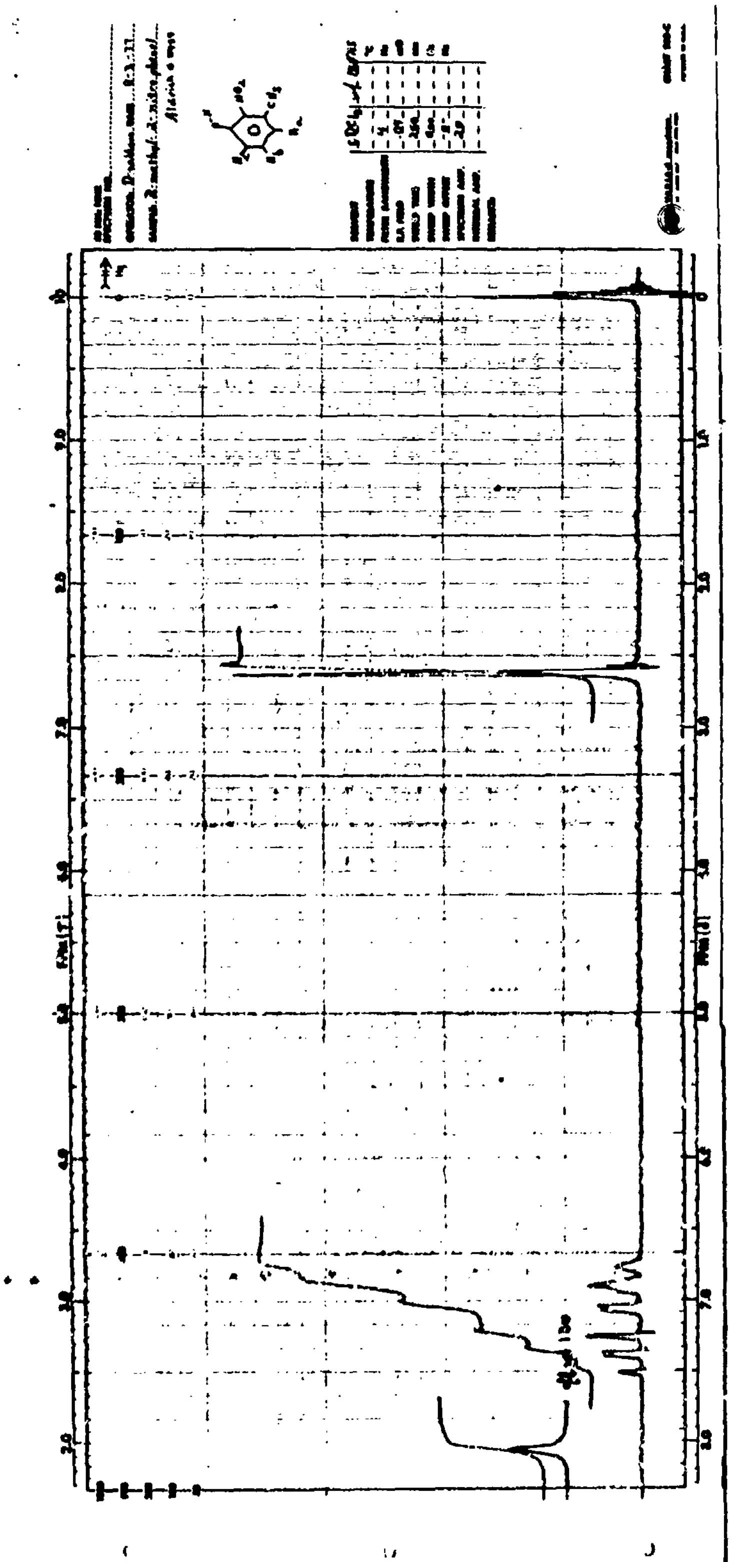


FIGURE 26 NMR SPECTRUM OF 3-METHYL-2-NITROPHENOL

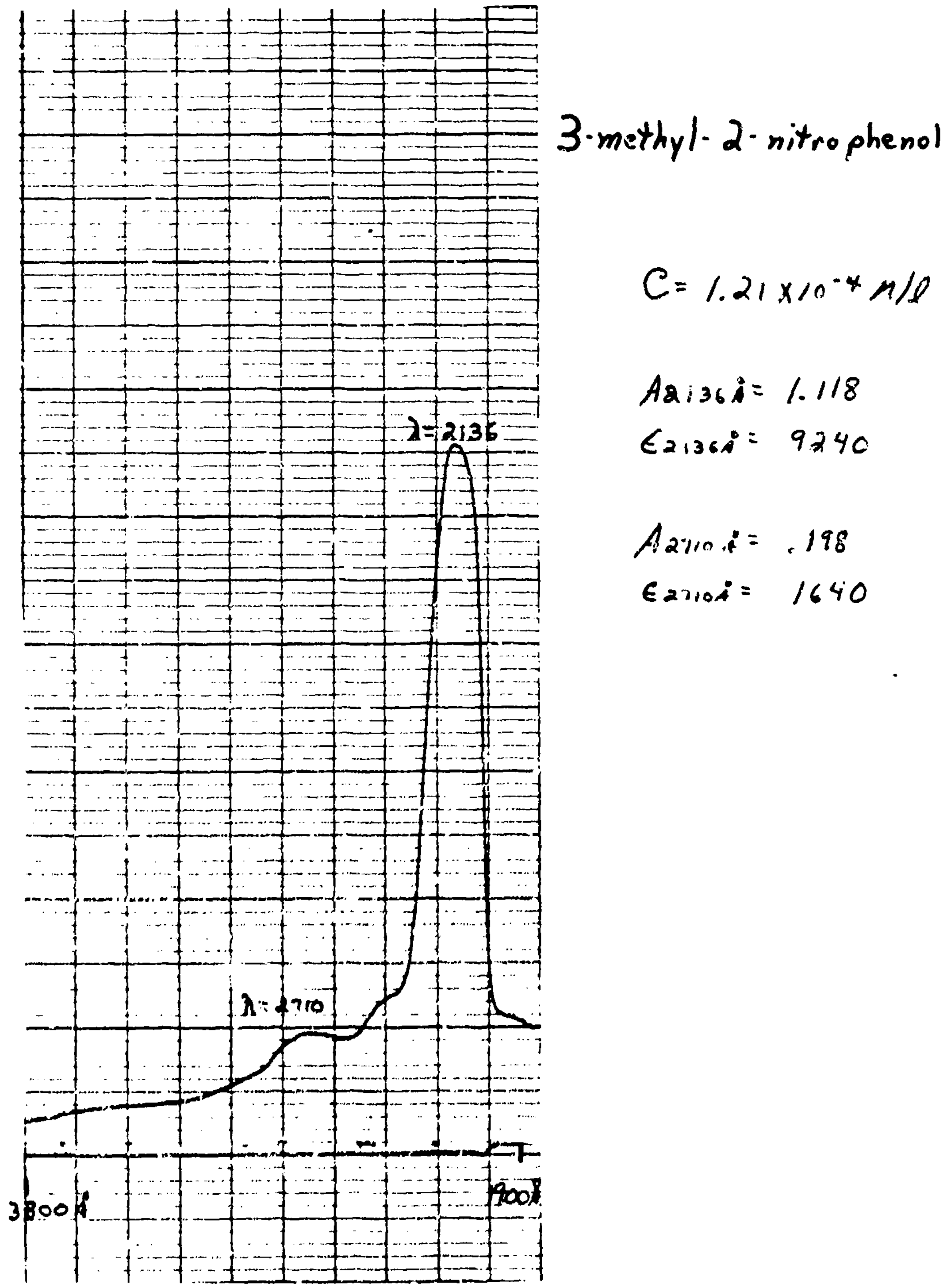


FIGURE 27 UV SPECTRUM OF 3-METHYL-2-NITROPHENOL

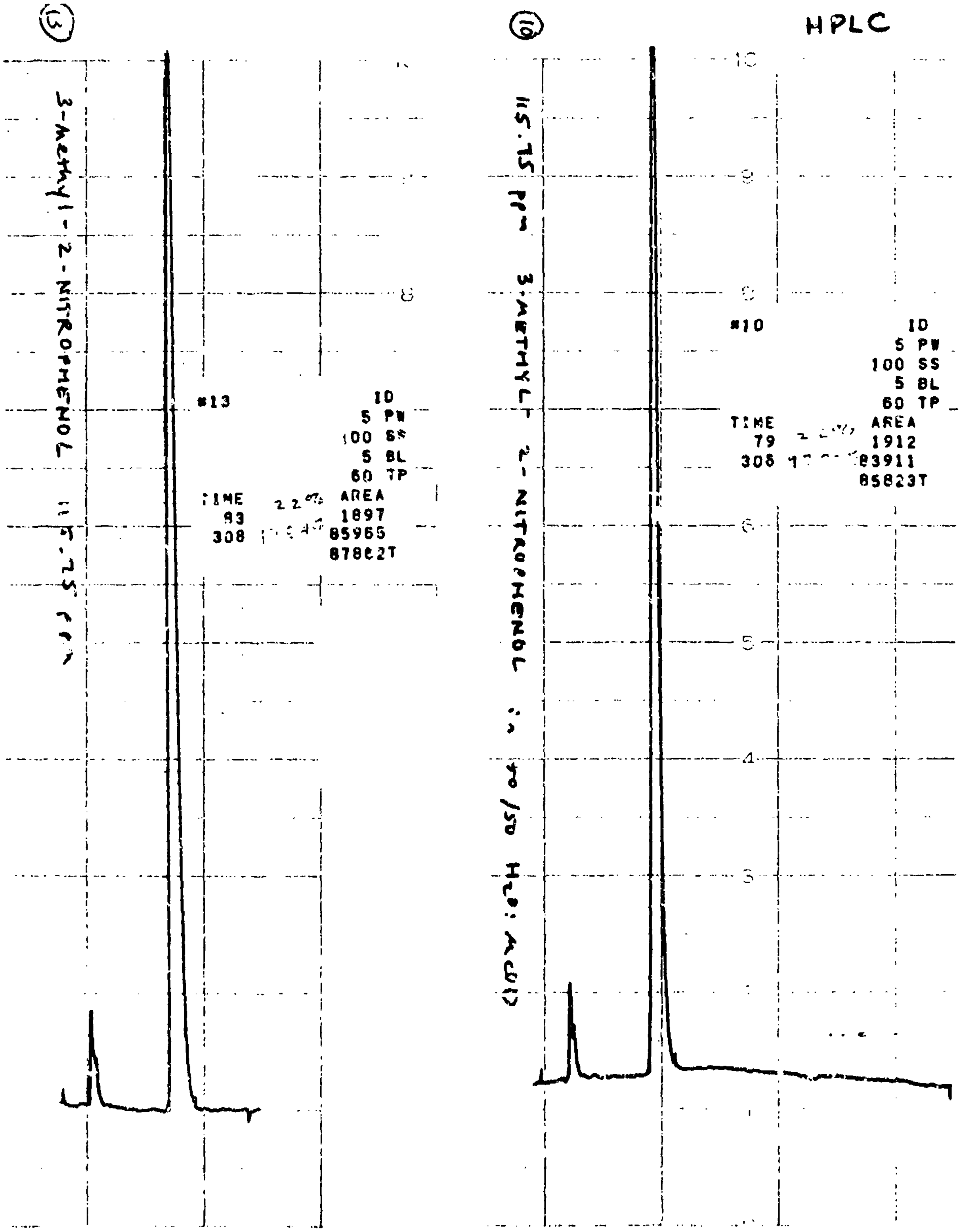


FIGURE 28 HPLC CHROMATOGRAM OF 3-METHYL-2-NITROPHENOL

GC

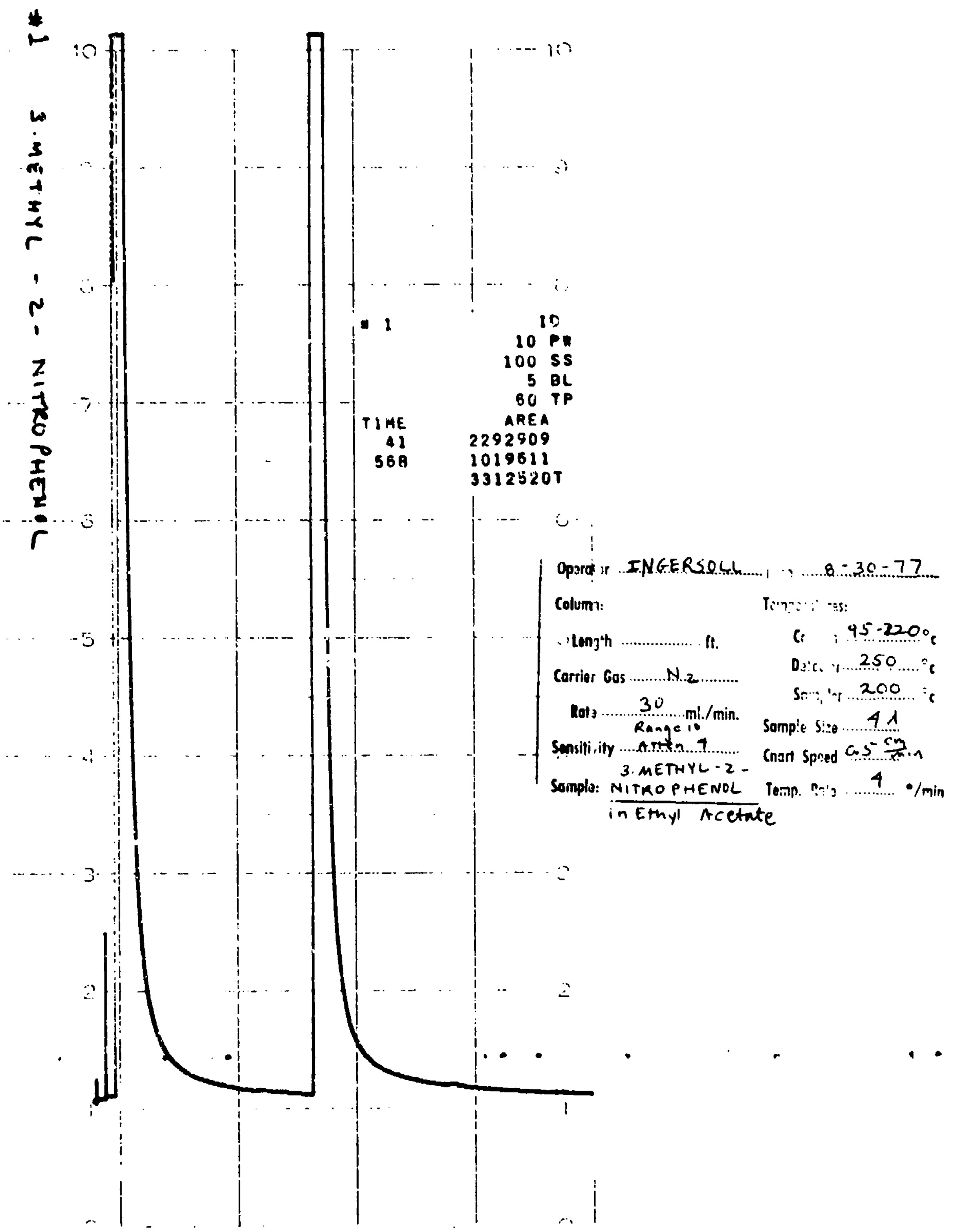


FIGURE 29 GC SPECTRUM OF 3-METHYL-2-NITROPHENOL

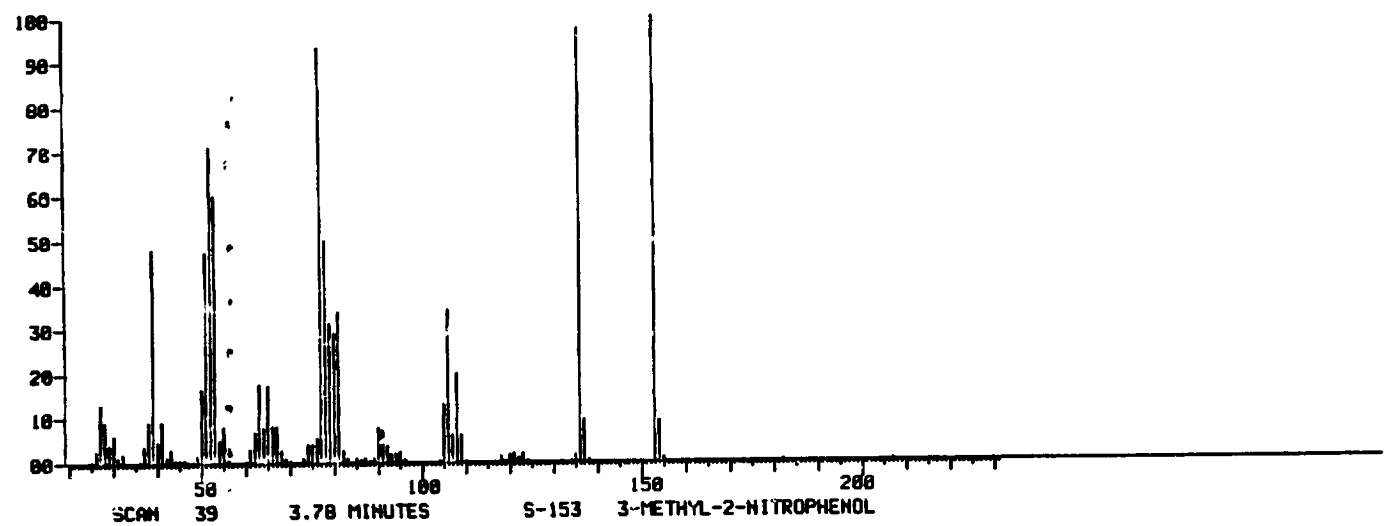
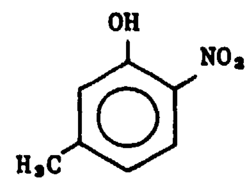


FIGURE 30 MASS SPECTRUM OF 3-METHYL-2-NITROPHENOL

4.5 5-Methyl-2-Nitrophenol
[700-38-9]



Source: Aldrich Chemical Company
Lot No. 122929
Catalog No. 13,779-0

Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 3.0 (intermolecular H-bonded O-H), 3.3 (C-H, aromatic), 6.3, 6.8 (C=C, ring), 8.5 (C-O), 11.4, 11.9 (C-N, aromatic NO_2), 9.25, 10.5, 12.2, 13.25, 13.65 μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.40 (singlet, 3H) CH_3; δ 6.77 (doublet, H, J = 9 cps) H_a
δ 6.93 (singlet, H) H_b; δ 7.97 (doublet, 0.1H, J = 9 cps) H_c
δ 10.57 (singlet, H) OH.

uv (Methanol)--λ_{max} = 214.5 nm, A = 1.287, ε = 13000
λ_{max} = 286.0 nm, A = 0.747, ε = 7560
λ_{max} = 348.0 nm, A = 0.390, ε = 3950.

Purity (99.65% ± 0.35)

Elemental Analysis--

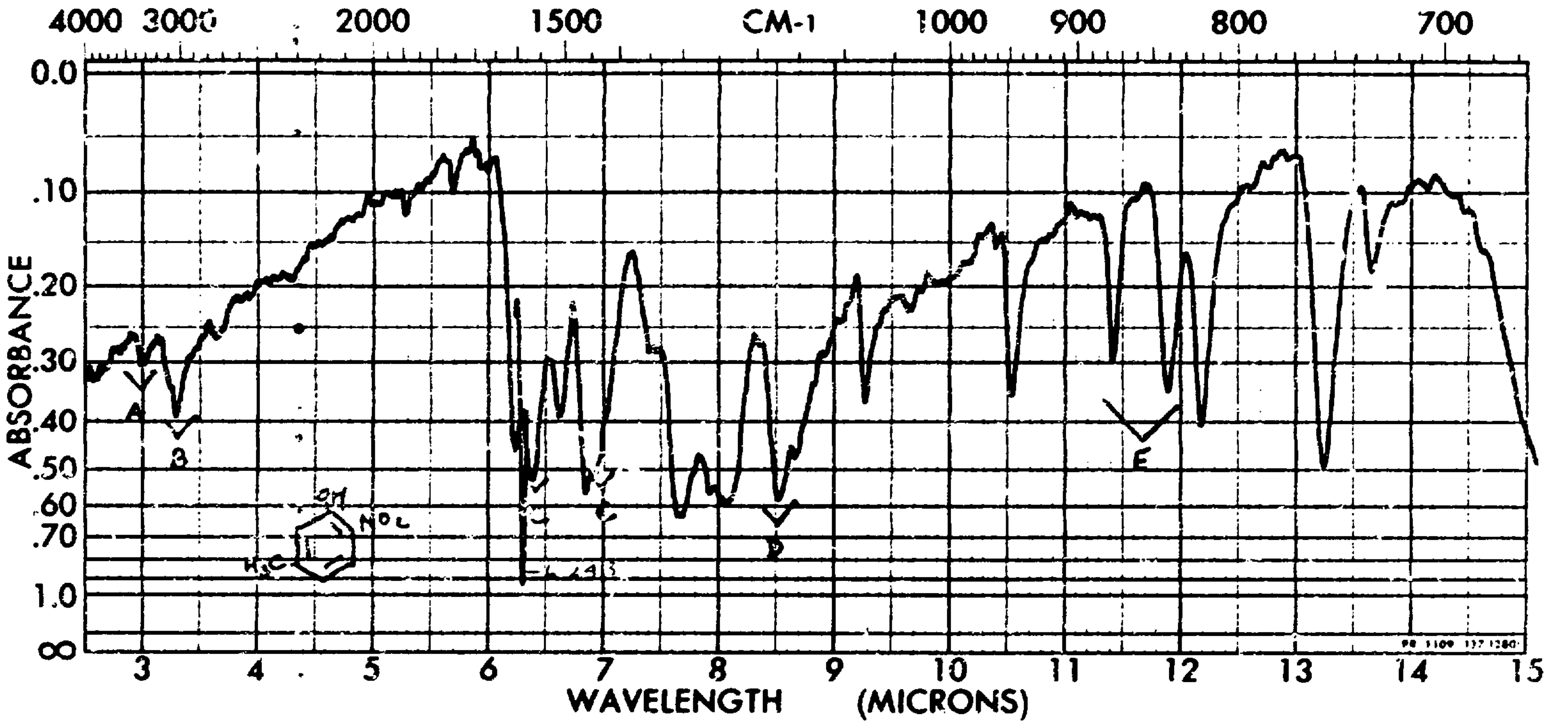
Anal. for $C_7H_7NO_3$: Calcd: C, 54.9; H, 4.61; N, 9.15
Found: C, 54.99 H, 4.59; N, 9.06.

High-Pressure Liquid Chromatography--One major component (representing 99.3% of total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 503 sec 5-methyl-2-nitrophenol 99.3%; 143 sec impurity 0.7%.

Gas Chromatography--One major peak (representing 100% of total peak areas) was observed by gc under the following conditions:

- Column: 5' x 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 95 to 220°C at 4°/min
- Flow rate: 30 ml/min N_2
- Detection: Flame ionization
- Retention time: 657 sec 5-methyl-2-nitrophenol 100%.



SPECTRUM NO.	ORIGIN	LEGEND A: O-H stretch intermolecularly H-bonded	REMARKS E. C-N stretch (aromatic NO_2)
SAMPLE 5-METHYL-2-NITROPHENOL KBr PELLET		1. B: Aromatic C-H stretch C: C=C ring stretch	
	PURITY	2. D C-O stretch	
Aldrich Chemical	PHASE	DATE AUGUST 22, 1977	
Lot No. 122927	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO.
SAMPLE

FIGURE 31 INFRARED SPECTRUM OF 5-METHYL-2-NITROPHENOL

RECORDING CHARTS

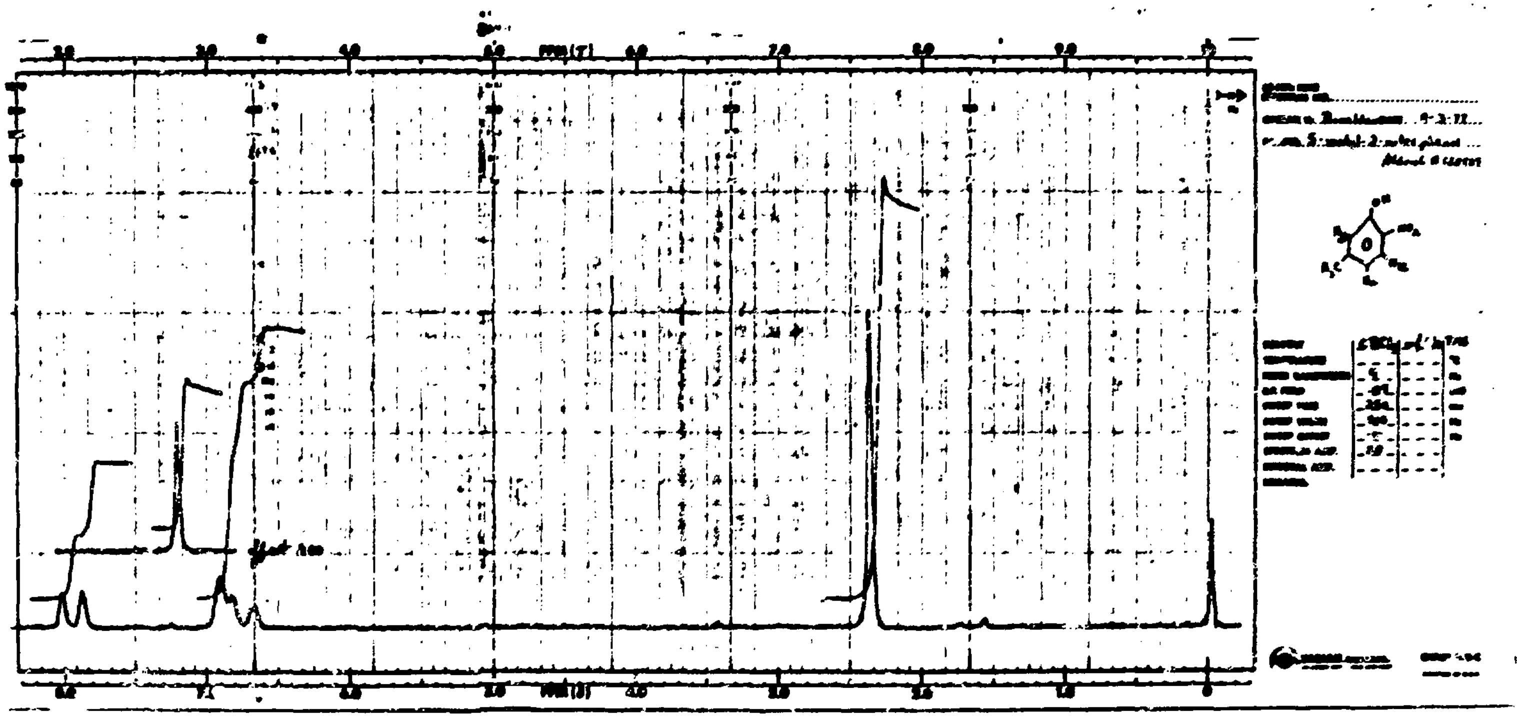


FIGURE 32 NMR SPECTRUM OF 5-METHYL-2-NITROPHENOL

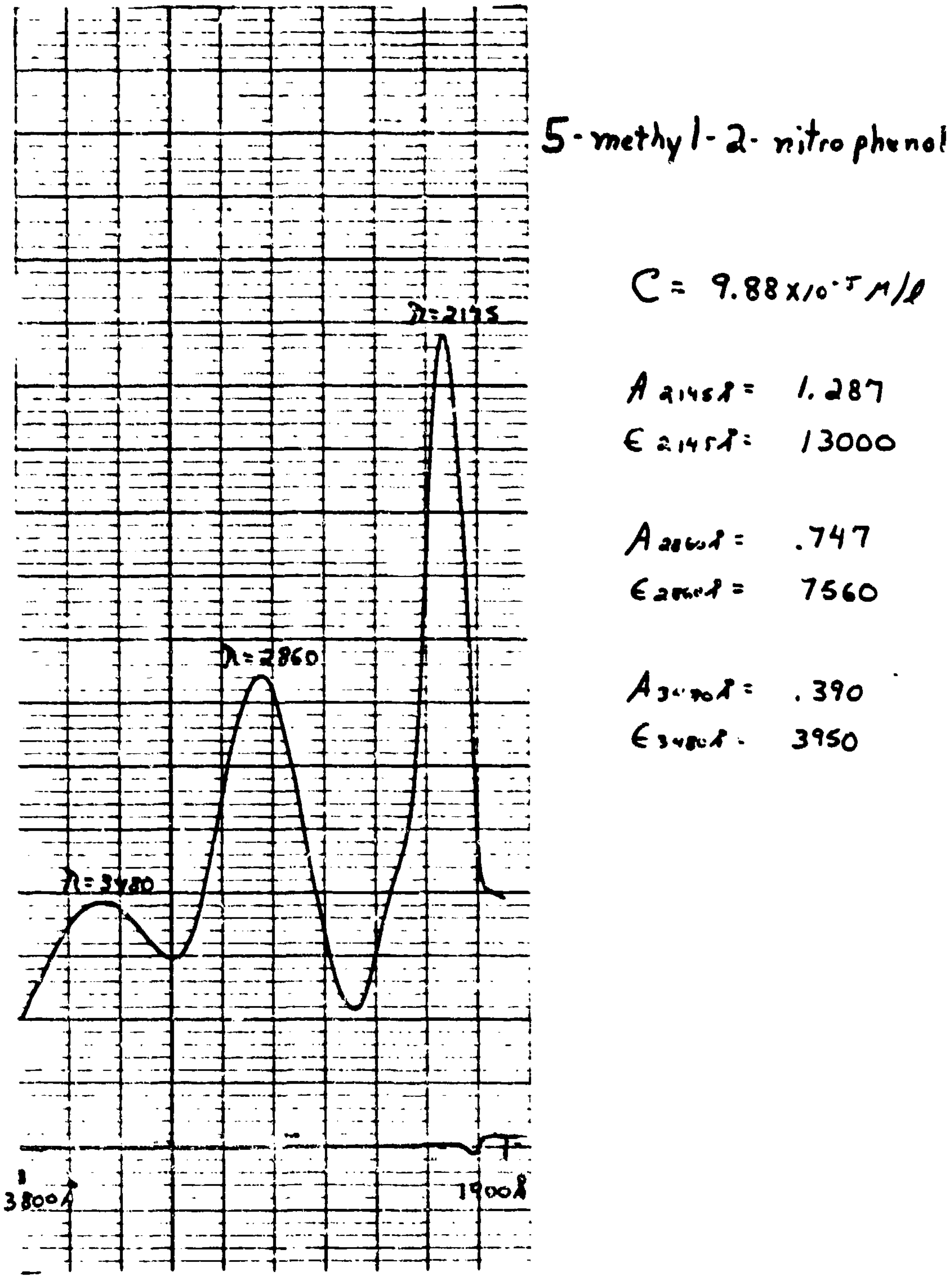


FIGURE 33 UV SPECTRUM OF 5-METHYL-2-NITROPHENOL

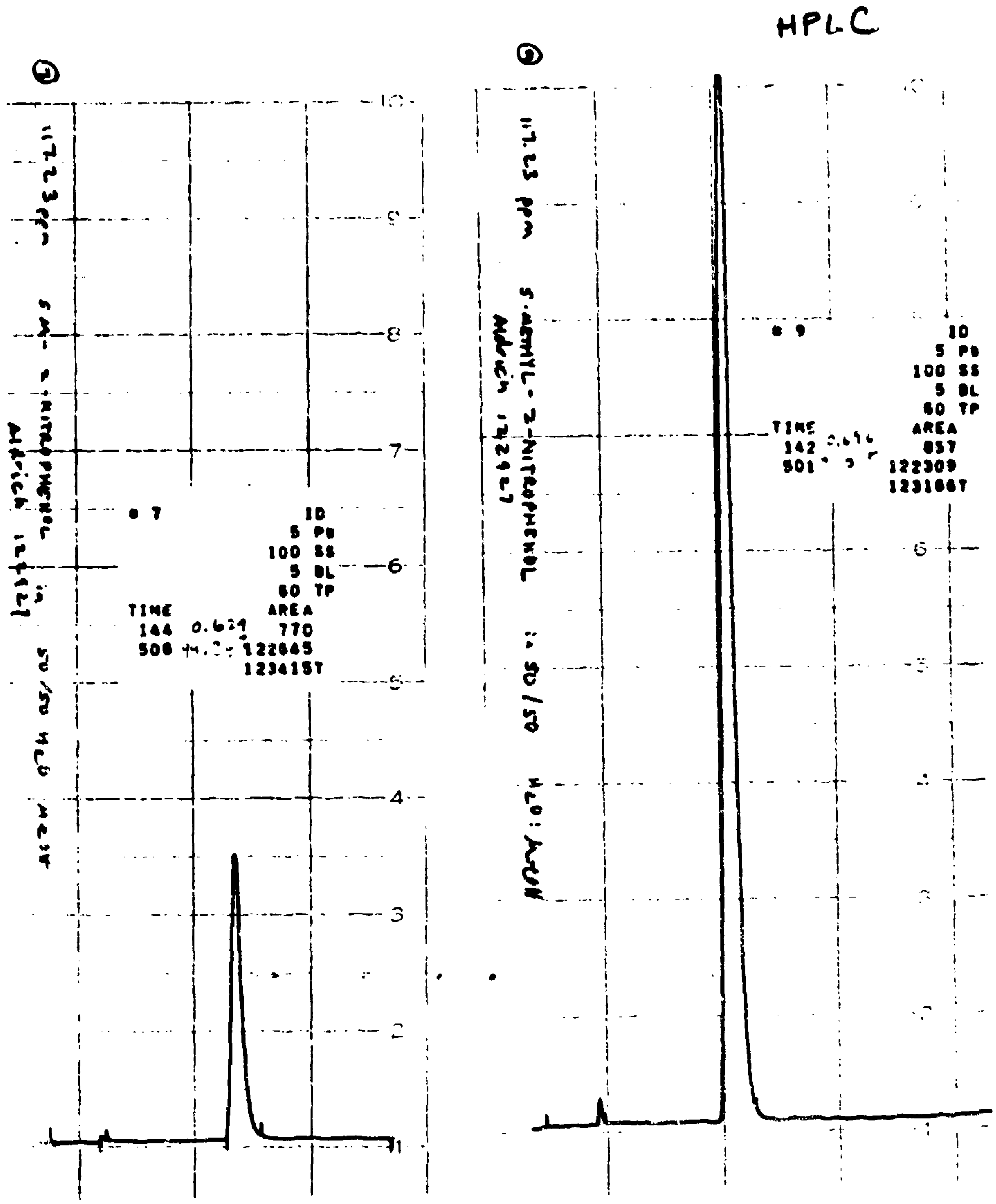


FIGURE 34 HPLC CHROMATOGRAM OF 5-METHYL-2-NITROPHENOL

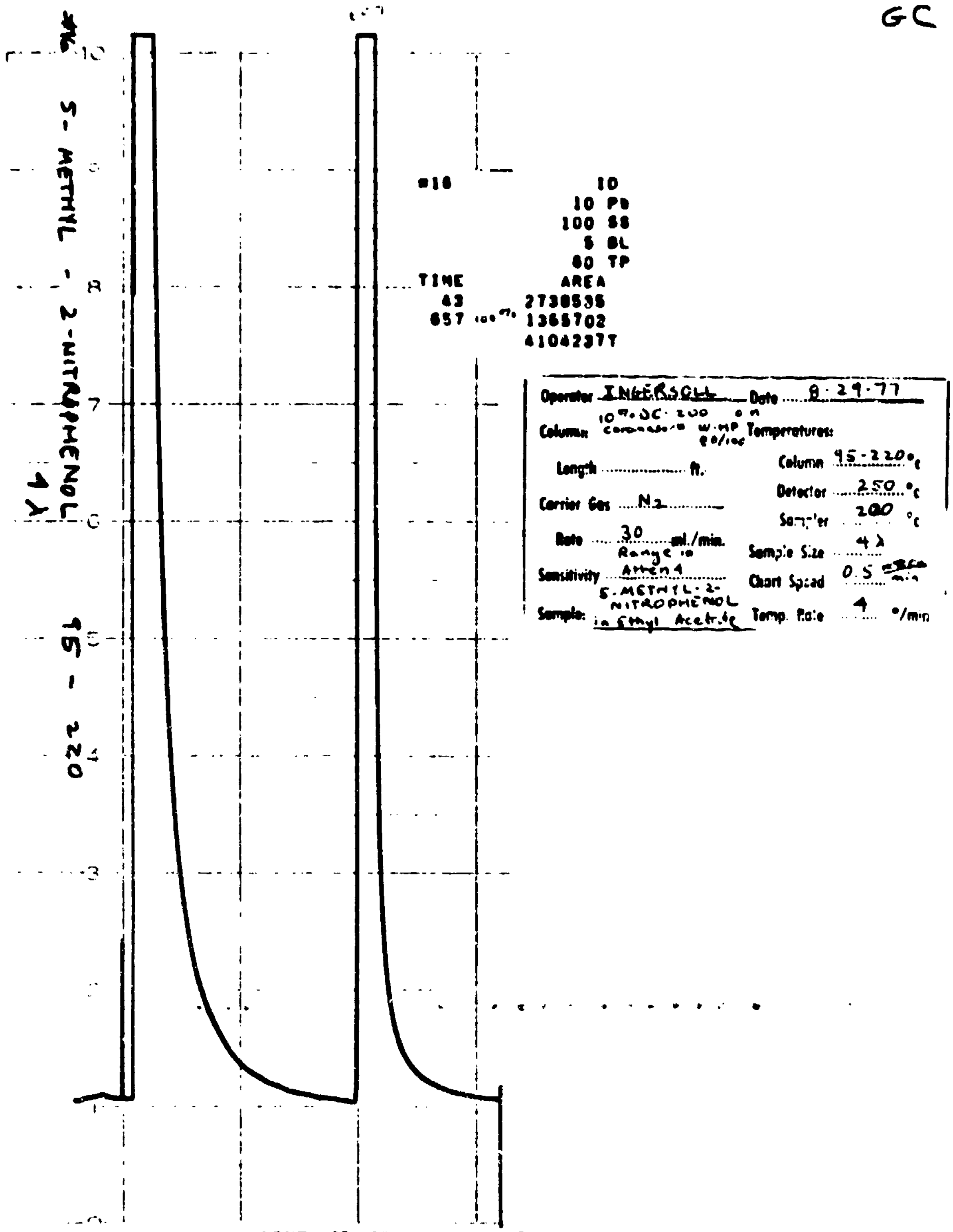


FIGURE 35 GC SPECTRUM OF 5-METHYL-2-NITROPHENOL

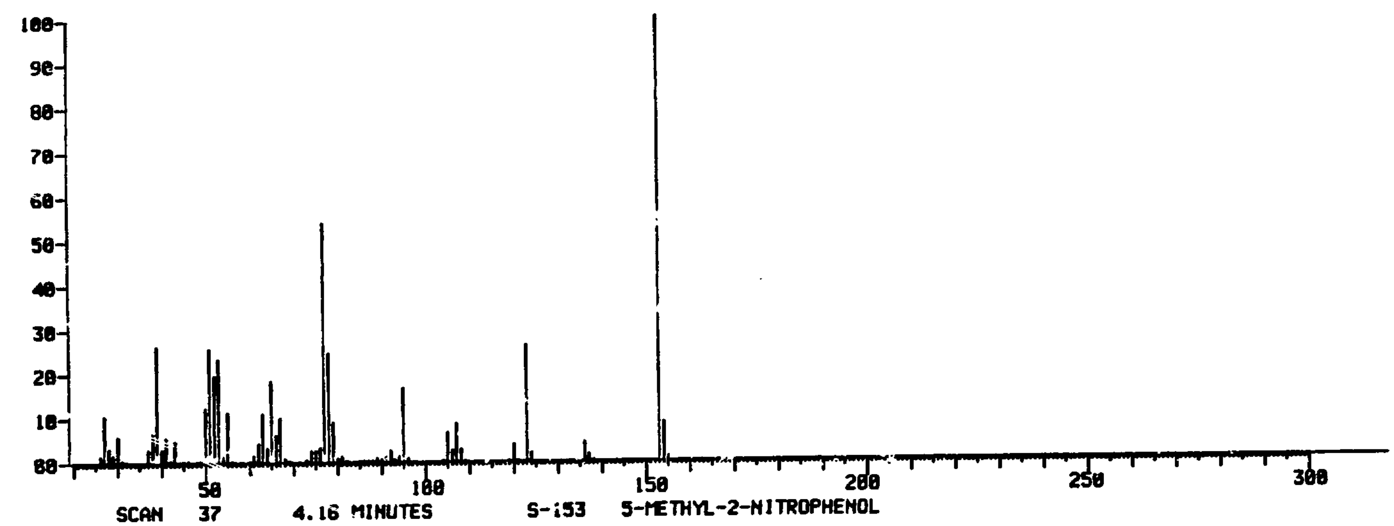
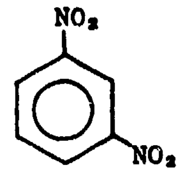


FIGURE 36 MASS SPECTRUM OF 5-METHYL-2-NITROPHENOL

4.6 1,3-Dinitrobenzene
[99-65-0]



Source: Eastman Organic Chemicals
Lot No. 601-344
Catalog number no longer available

Identity

Ir--The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference No. 81 for m-dinitrobenzene (KBr wafer). The following bands were observed:

(1) (KBr pellet) 3.25 (C-H, aromatic), 6.2, 6.8 (C=C, ring), 6.5, 7.4 (N=O) 9.35 (C-H), 11.9 (C-N, aromatic NO_2), 10.9, 12.2, 13.7, 14.0 µm.

(2) (Thin film in $CHCl_3$), 3.5 (C-H, of $CHCl_3$), 5-6 (aromatic overtones--possibly not all meta-benzenoid substitution) µm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 7.85 (triplet, 1H, J = 8 cps) H_a
δ 8.55 (doublet of doublets, 2H, J = 8 cps, J = 2 cps) H_b
δ 9.05 (doublet of doublets 1 H, J = 2 cps, J = 2 cps) H_c.

uv (methanol--λ_{max} = 233.8 nm, A = 1.354, ε = 17700.

Purity (100%)

Elemental Analysis--

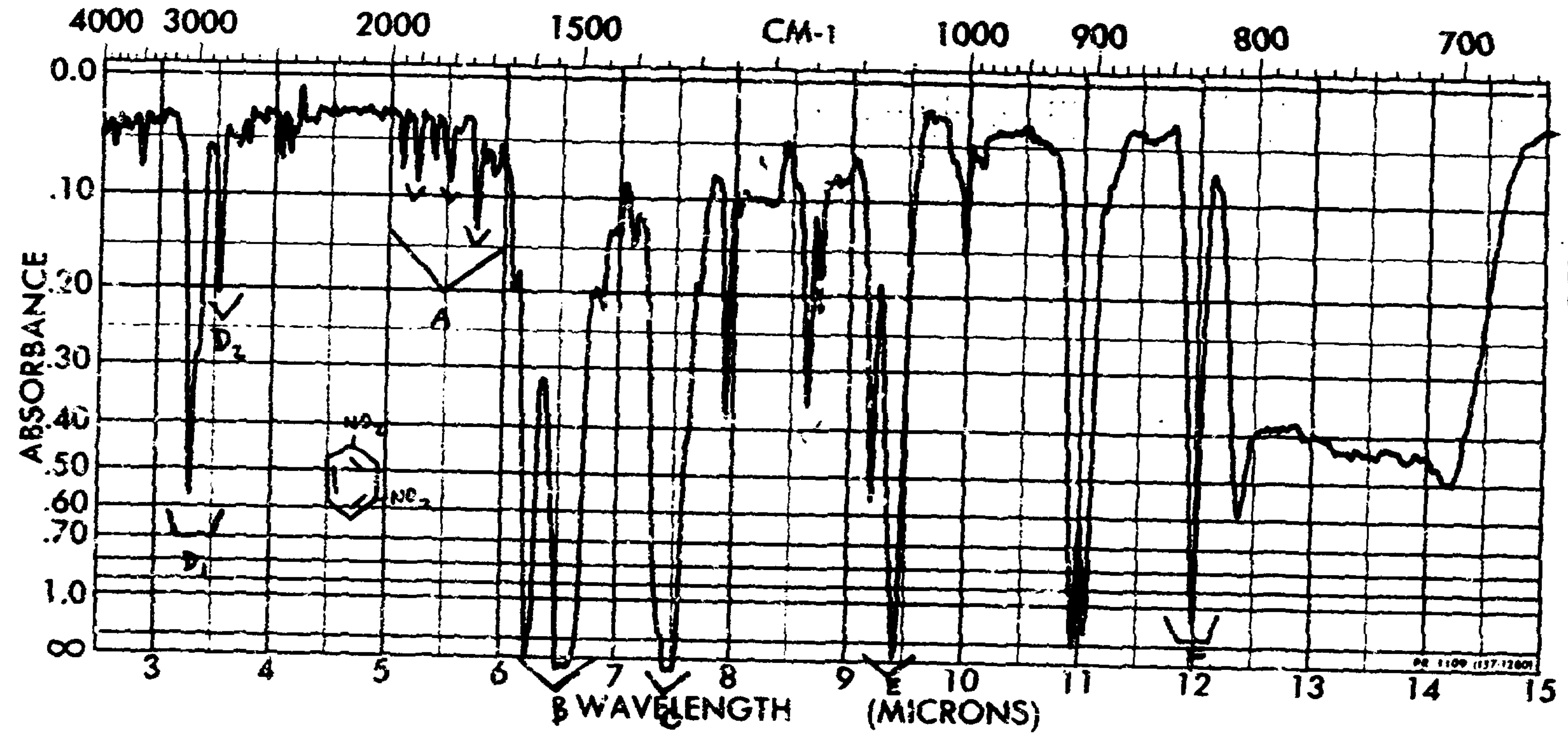
Anal. for $C_6H_4N_2O_4$: Calcd: C, 42.9; H, 2.4; N, 16.7
Found: C, 42.65; H, 2.43; N, 16.43.

High-Pressure Liquid Chromatography--One peak representing 100% of the total peak area was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 382 sec 1,3-dinitrobenzene 100%.

Gas Chromatography--One peak (representing 100% of the total peak areas) was observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 8/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 607 sec 1,3-dinitrobenzene 100%.



SPECTRUM NO. 3	ORIGIN	LEGEND A: overtones - possibly not all meta	REMARKS
SAMPLE m-DINITROBENZENE in $CHCl_3$	REF. CELL : $CHCl_3$	1. B: N=O asymmetric & C=C ring stretch	
	PURITY	C: N=O symmetric	E: In plane C-H bend
EASTMAN LOT # 601-344	PHASE	2. D_1: Aromatic C-H stretch. D_2: Methyl C-H stretch - $CHCl_3$	F: Possibly Ar-NO_2 C-N stretch
	THICKNESS	DATE MAY 23, 1977	
		OPERATOR C. INGERSOLL	

SPECTRUM NO. 5
SAMPLE

FIGURE 37 INFRARED SPECTRUM OF 1,3-DINITROBENZENE

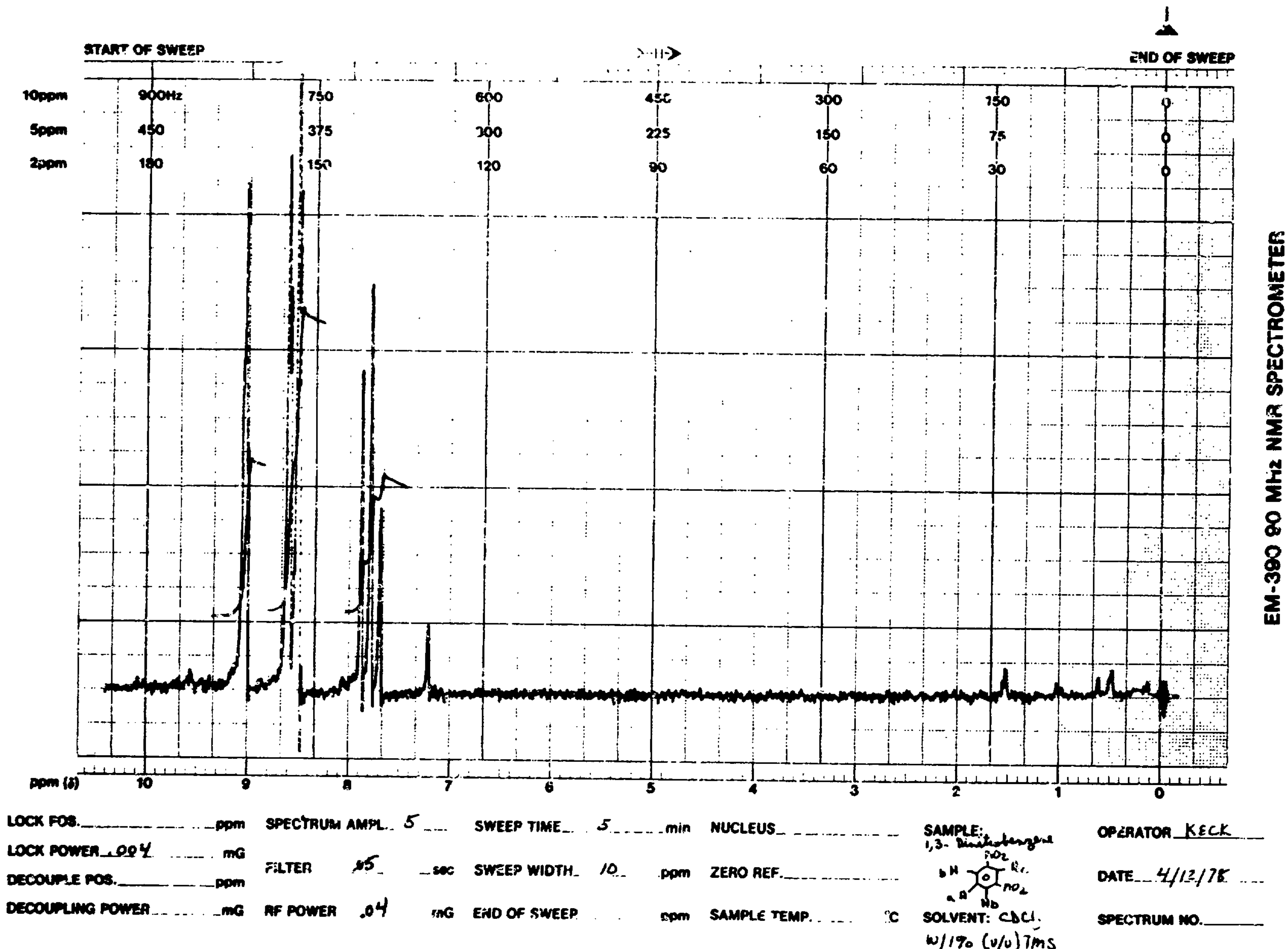
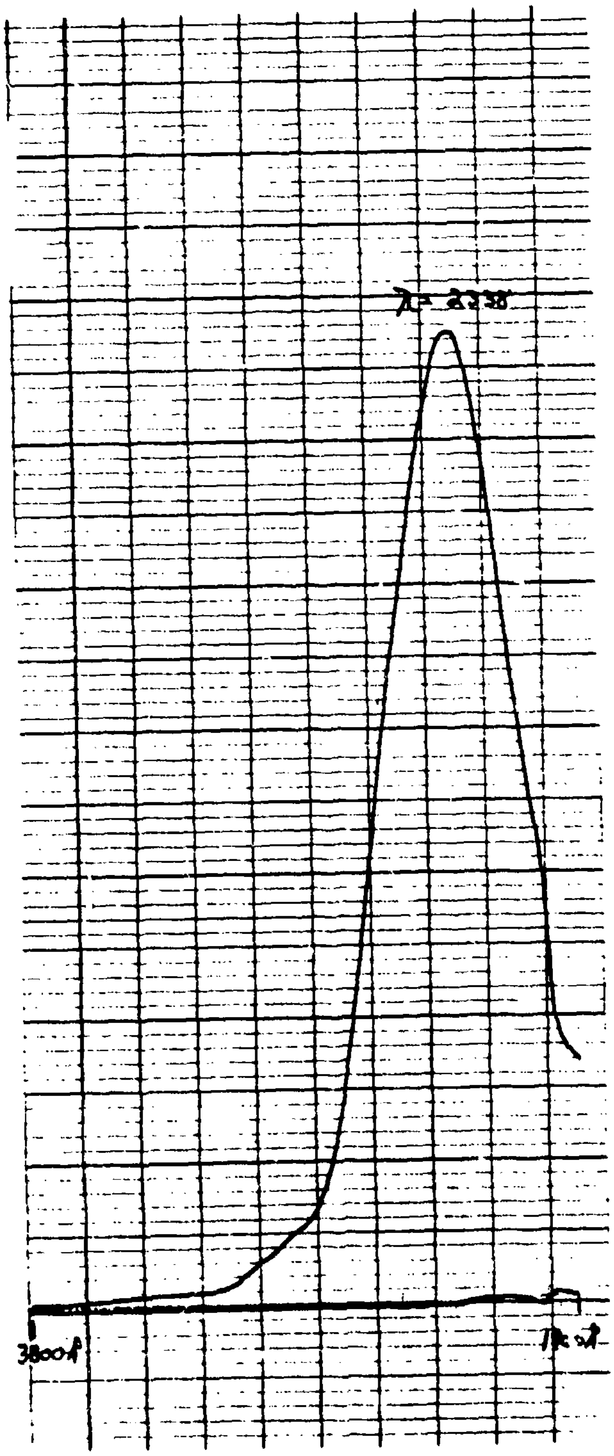


FIGURE 38 NMR SPECTRUM OF 1,3-DINITROBENZENE



1,3-dinitrobenzene

$C = 7.64 \times 10^{-5}$ M/l

$A_{2338Å} = 1.354$

$\epsilon_{2338Å} = 17700$

FIGURE 39 UV SPECTRUM OF 1,3-DINITROBENZENE

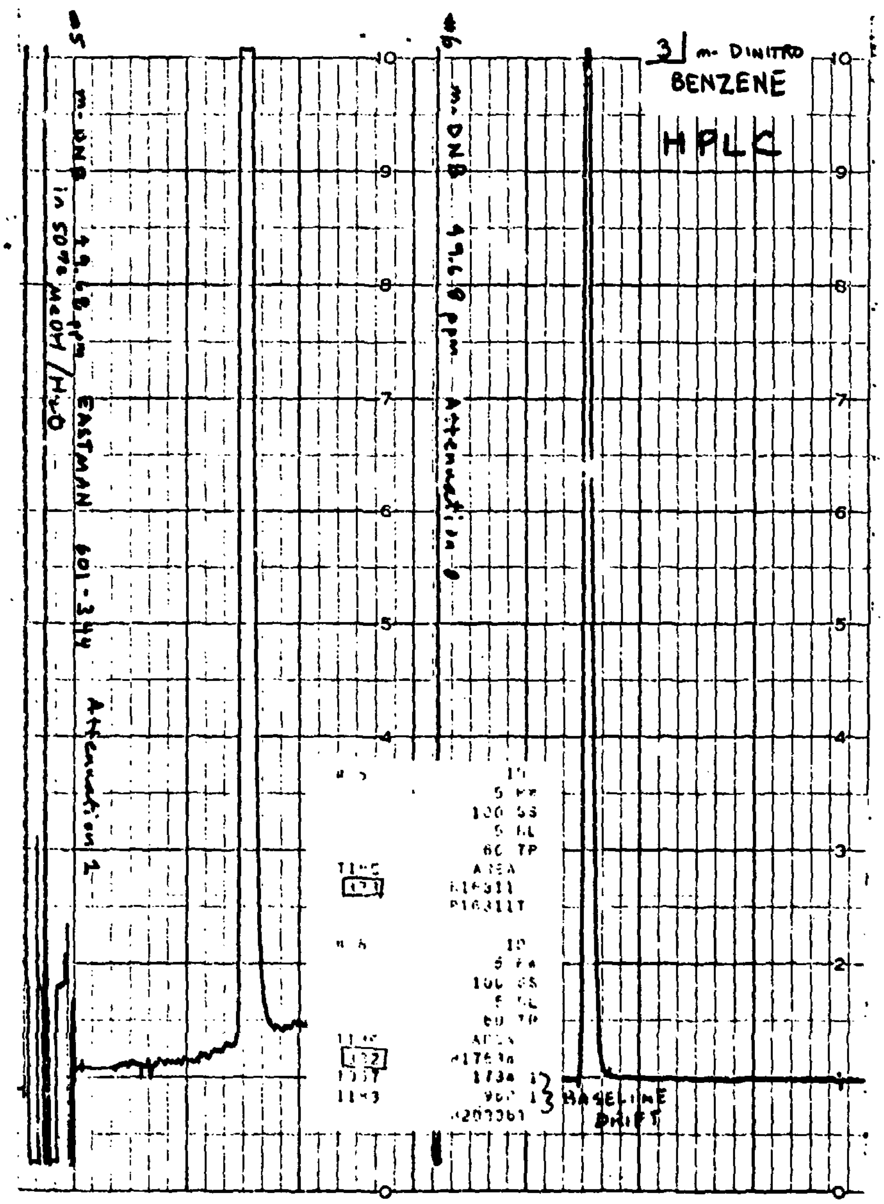
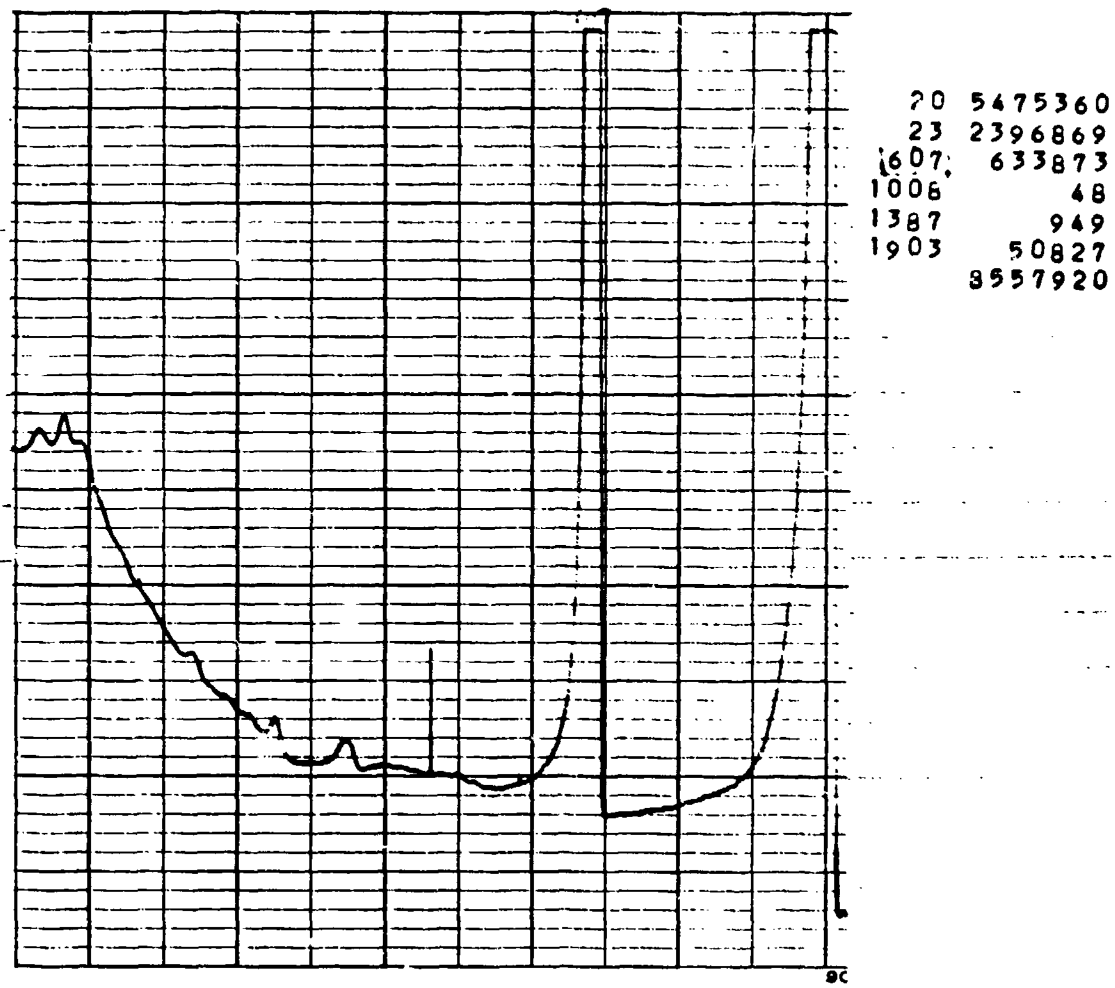


FIGURE 40 HPLC CHROMATOGRAM OF 1,3-DINITROBENZENE

GC

meta-Dinitrobenzene



Operator Donaldson Date 3-23-77

Column: [redacted]

Temperatures:

Length 5 ft.

Column 100-220 °c

Carrier Gas N_2

220 °c

200 °c

Rate 20

2 µl

Sensitivity 10^{-10}, Atten 1

16 in/min

Sample: m-DNB

4 °/min

FIGURE 41 GC SPECTRUM OF 1,3-DINITROBENZENE

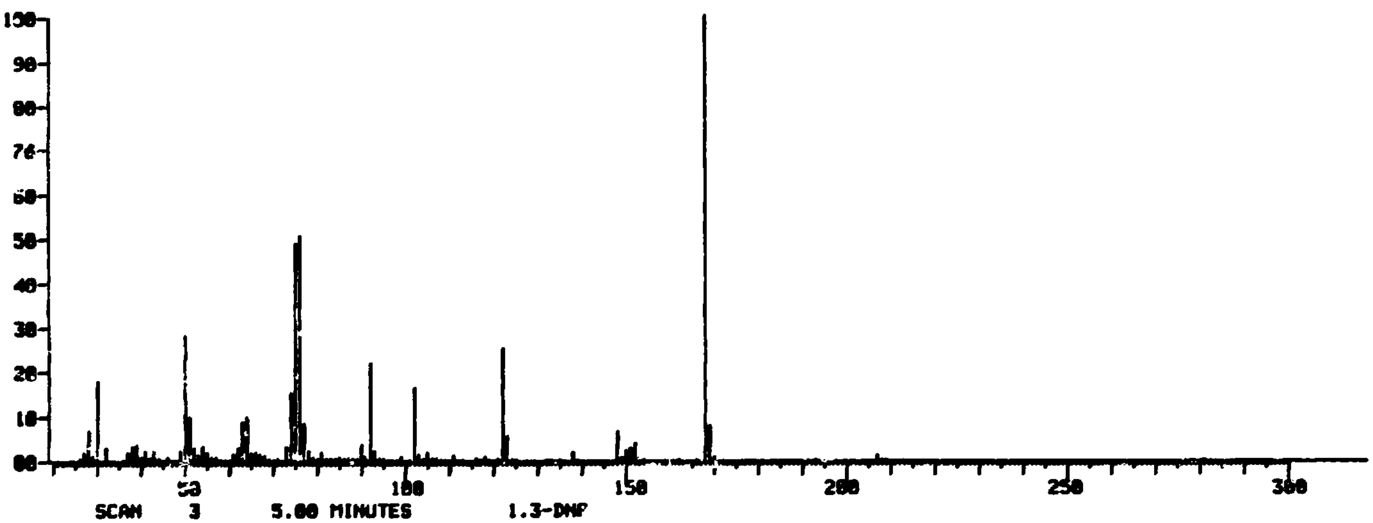
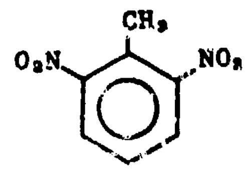


FIGURE 42 MASS SPECTRUM OF 1,3-DINITROBENZENE

4.7 <u>2,6-Dinitrotoluene</u>
2-Methyl-1,3-dinitrobenzene
[606-20-2]



Source: Aldrich Chemical Company
Lot No. 031947
Catalog No. D20,060-3

<u>Identity</u>

<u>Ir</u>—The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference No. 17378 for 2,6-dinitrotoluene (KBr wafer). The following bands were observed:

(1) (KBr pellet) 3.3, (=C-H, aromatic), 6.2, 6.9 (C=C, ring), 6.5, 7.4 (N=O), 11.85 (C-N, aromatic NO_2), 13.7 (C-H), 8.3, 9.2, 10.1, 11.15, 12.15, 14.1 µm.

(2) (Thin film in $CHCl_3$) 5-6 (aromatic overtones) µm.

<u>Nmr</u>--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.60 (singlet, 3H) CH_3; δ 7.57 (triplet, H, J = 8 cps) H_b;
δ 8.03 (doublet, 2H, J = 9 cps) H_a.

<u>uv (Methanol)</u>--λ_{max} = 207.4 nm, A = 0.770, ε = 13600
λ_{max} = 232.0 nm, A = 0.591, ε = 10400.

<u>Purity</u> (99.5% ± 0.5)

<u>Elemental Analysis</u>—

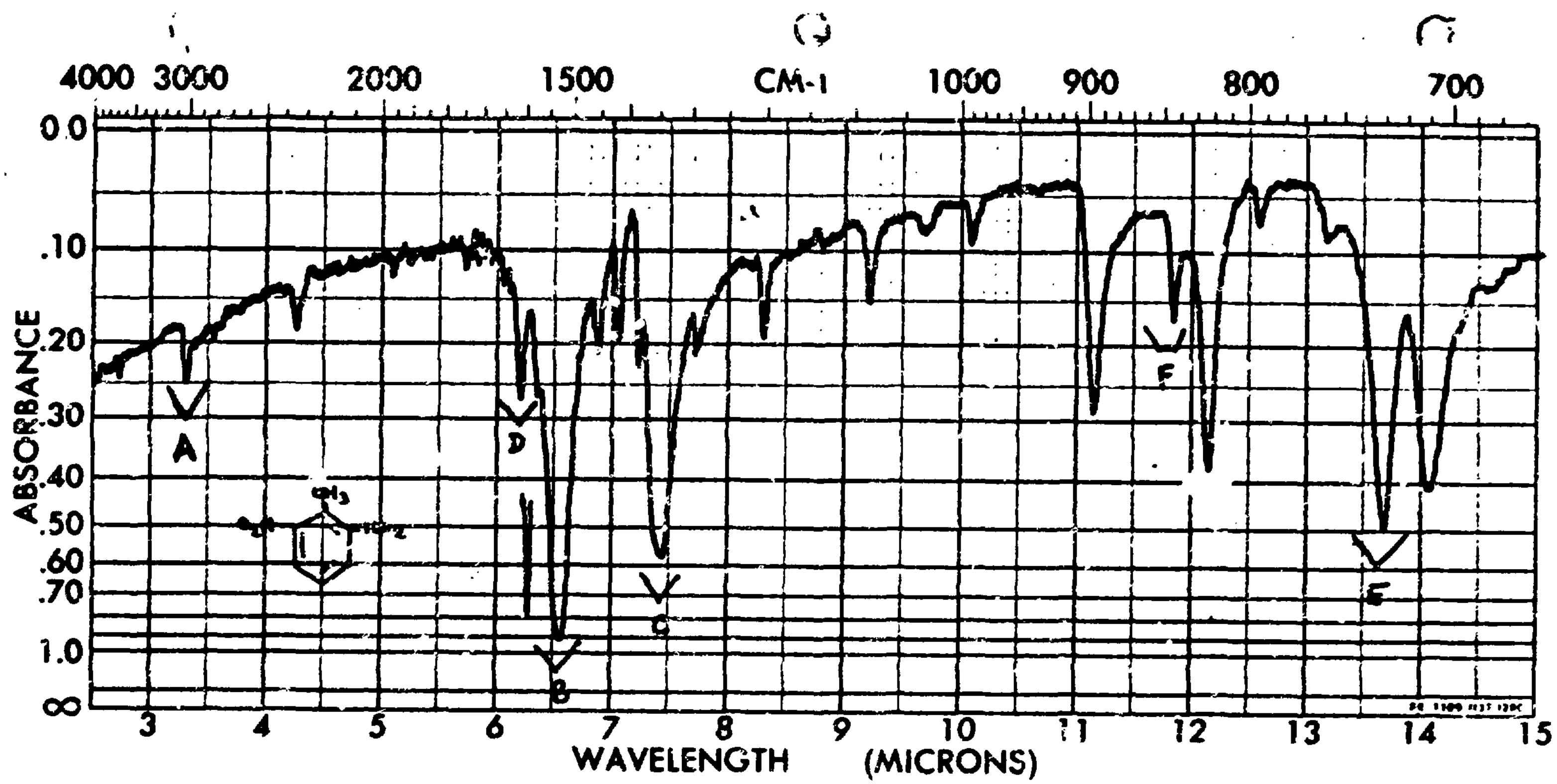
Anal. for $C_7H_6N_2O_4$: Calcd: C, 46.2; H, 3.3; N, 15.4
Found: C, 46.00; H, 3.30; N, 15.46.

High-Pressure Liquid Chromatography--One peak (representing 100% of the total peak areas) was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow Rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 506 sec 2,6-dinitrotoluene 100%.

Gas Chromatography--One major component (representing 99% of the total integrated peak areas) and one minor component were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 200°C at 4° /min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 649 sec 2,6-dinitrotoluene 99.0%; 773 sec impurity 1.0%.



SPECTRUM NO. 4	ORIGIN	LEGEND A: Aromatic C-H	REMARKS Slow SLIT : 1
SAMPLE 2,6-DINITROTOLUENE (KBr PELLET)		1. B: N=O stretch asymmetric	
		C: N=O stretch symmetric	
	PURITY	2. D: C=C ring stretch	
ID: Aldrich LOT NO. 031947 LOT SRI #1		E: out of plane C-H bend	
	PHASE	DATE MAY 11, 1977	F: [illegible]
	THICKNESS	OPERATOR INGERSOLL	

SPECTRUM NO.
SAMPLE

FIGURE 43 INFRARED SPECTRUM OF 2,6-DINITROTOLUENE

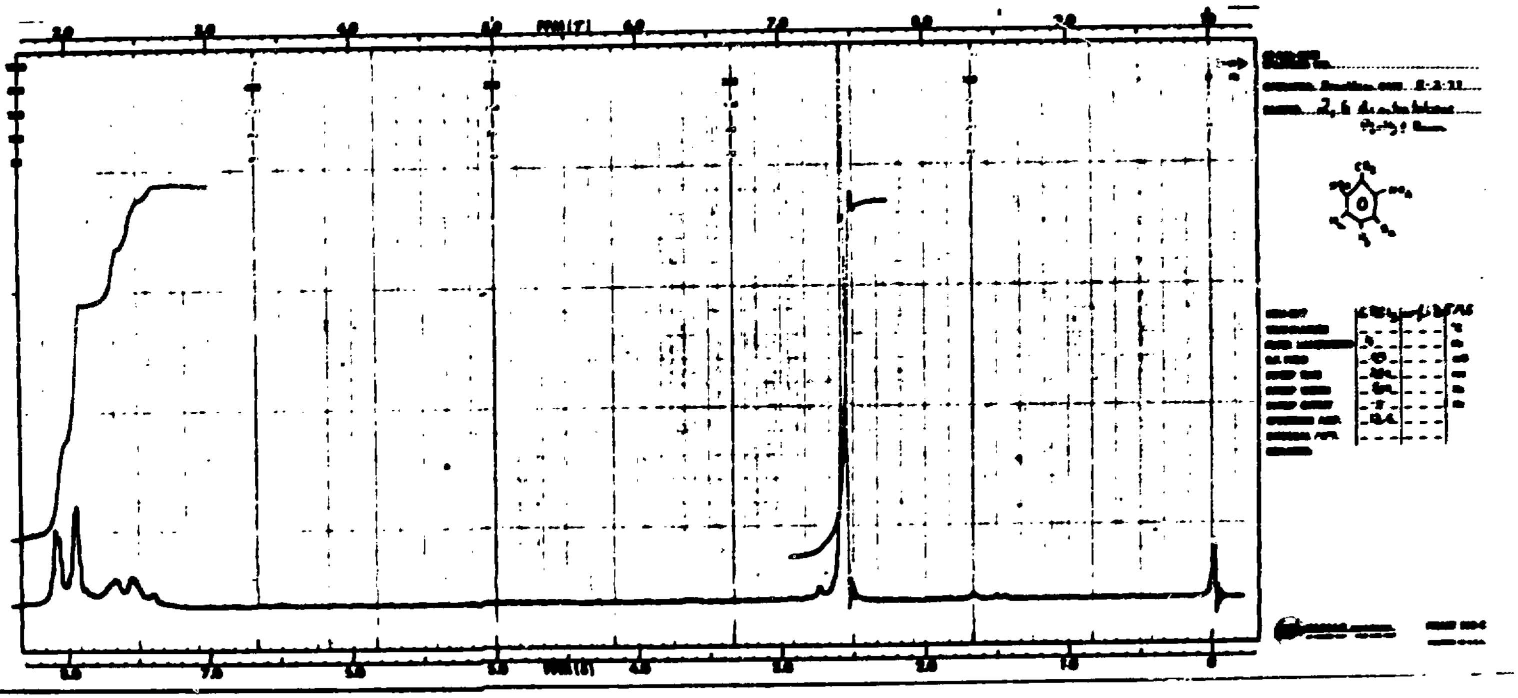
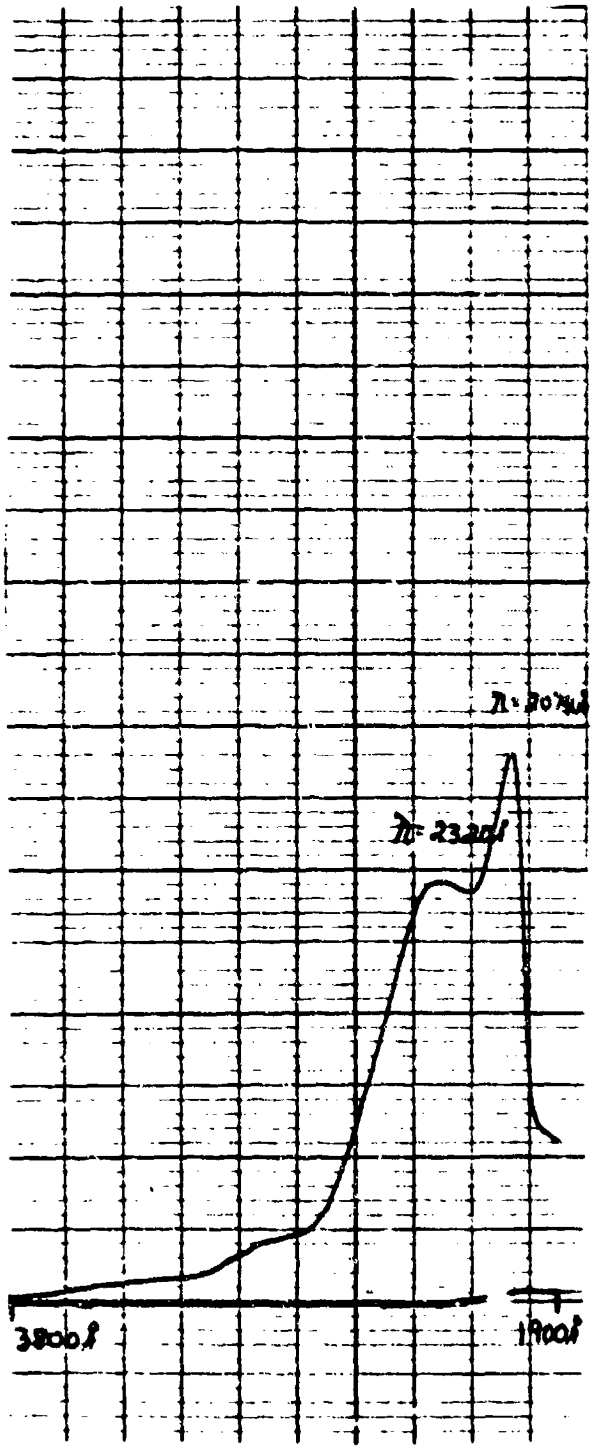


FIGURE 44 NMR SPECTRUM OF 2,6-DINITROTOLUENE



2,6-dinitrotoluene

$C = 5.66 \times 10^{-5}$ M/l

$A_{2074Å} = .770$

$\epsilon_{2074Å} = 13600$

$A_{2320Å} = .591$

$\epsilon_{2320Å} = 10400$

FIGURE 45 UV SPECTRUM OF 2,6-DINITROTOLUENE

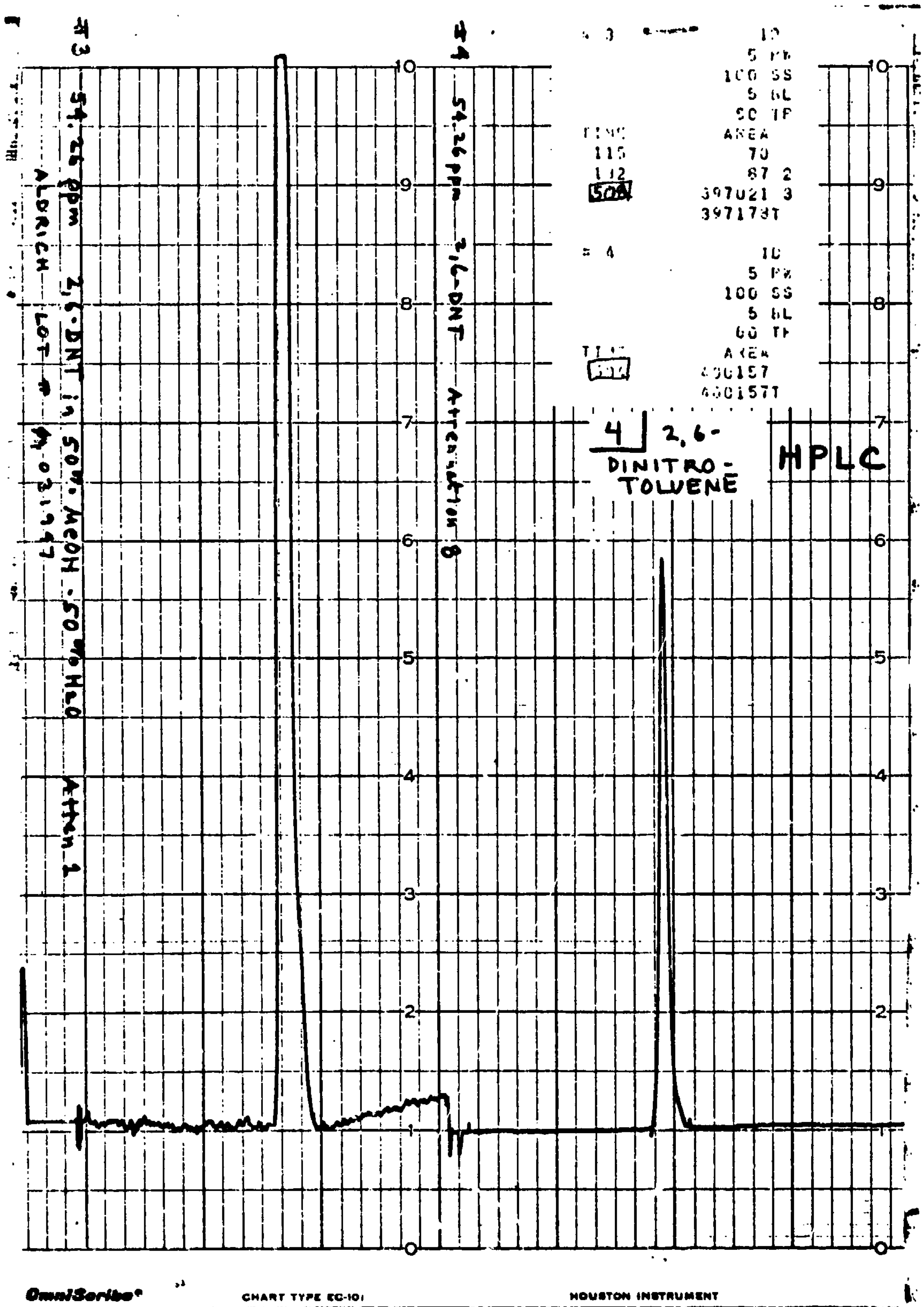
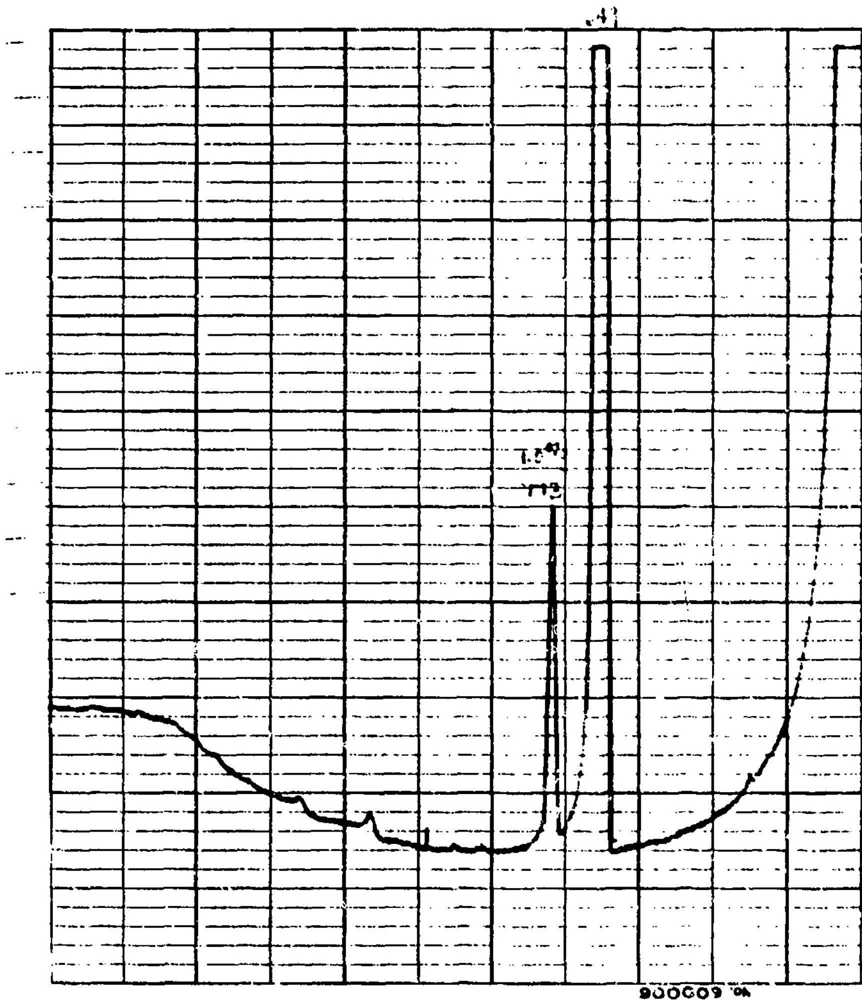


FIGURE 46 HPLC CHROMATOGRAM OF 2,6-DINITROTOLUENE

GC

2,6 Dinitrotoluene



21	7786367
649	626512
773	6666
2151	4
2211	
	8421530

Operator Donaldson Date 3-24-77

Column: [redacted]

10% DC 200 on HP 80/100

Length 5 ft.

Carrier Gas N_2

Rate 20 ml/min.

Sensitivity 10^{-10}, Attn 1

Sample: 2,6 - DNT

Temperature:

Column 150-220°C

Detector 220 °C

Sample Inj 200 °C

Sample Size 2ul

Chart Speed 1/6 in/min

Temp. Rate 4 °/min.

FIGURE 47 GC SPECTRUM OF 2,6-DINITROTOLUENE

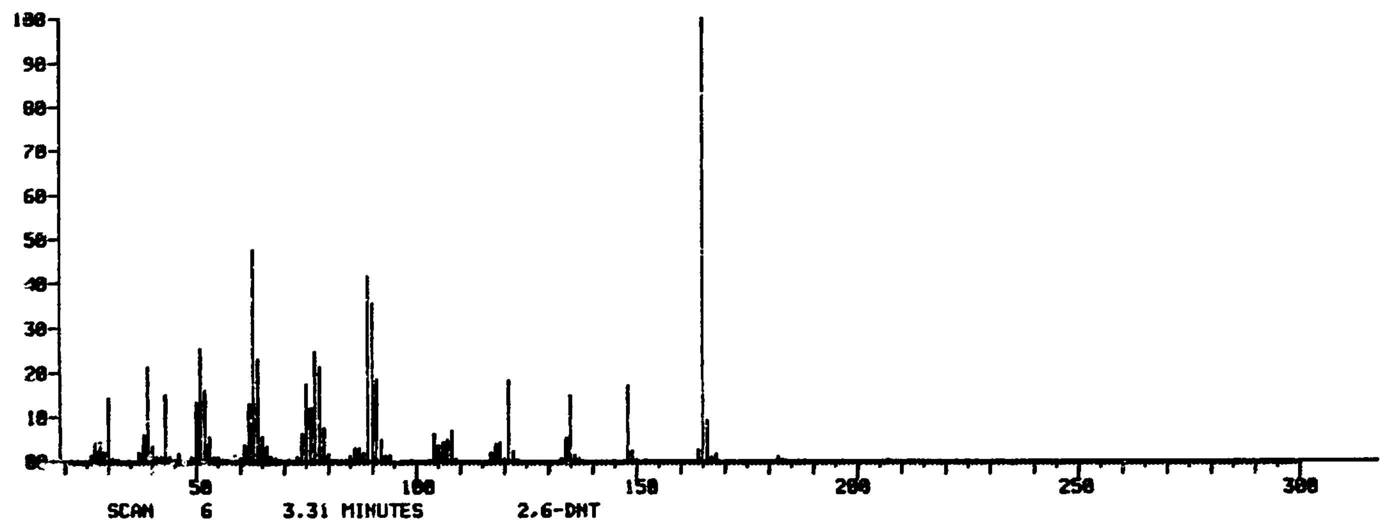
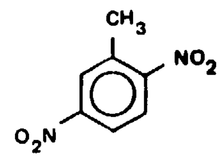


FIGURE 48 MASS SPECTRUM OF 2,6-DINITROTOLUENE

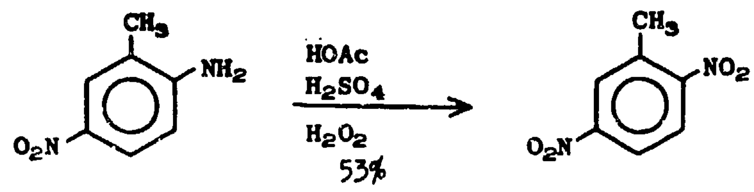
4.8 2,5-Dinitrotoluene

2-Methyl-1,4-dinitrobenzene

[619-15-8]



Source: Synthesis, SRI



Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed:

(1) (KBr pellet) 3.3 (=C-H, aromatic), 3.5 (C-H, methyl), 6.5, 7.4 (N=O), 6.8 (C=C, ring) 9.68, 13.7 (C-H), 11.7, 11.9 (C-N stretch, aromatic NO_2), 7.1, 8.7, 9.0, 10.7, 11.1, 12.48 μm.

(2) (Thin film in $CHCl_3$) 5-6 (aromatic overtones) μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.70 (singlet, 3H) CH_3; δ 8.22 (multiplet, 3H) H.

uv (Methanol)--λ_{max} = 207.0 nm, 1.405, ϵ = 16,000

λ_{max} = 238.2 nm, A = 0.972, ϵ = 11,500

λ_{max} = 300.0 nm, A = 0.205, ϵ = 2420.

Purity (99.99% ± 0.1)

Elemental Analysis--

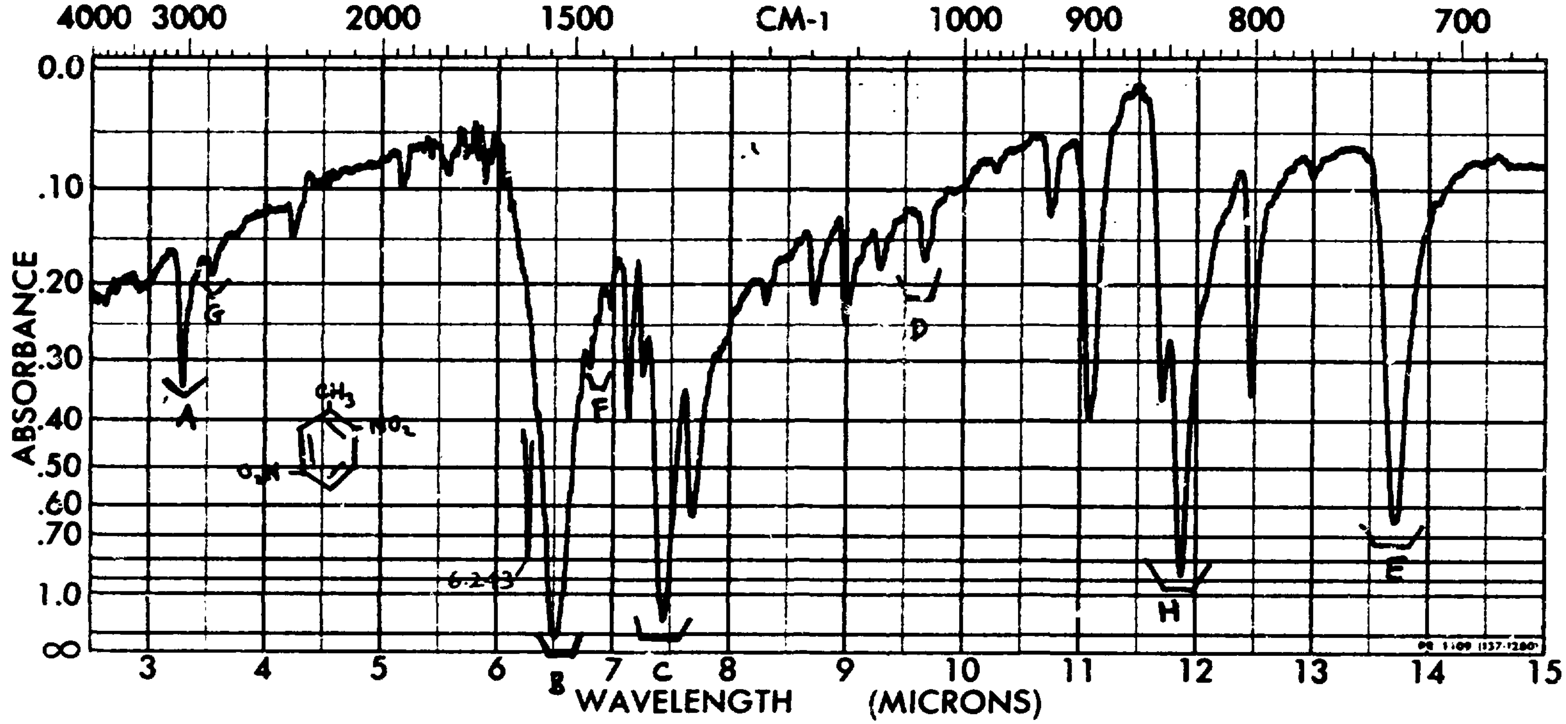
Anal. for $C_7H_6N_2O_4$: Calcd: C, 46.2; H, 3.3; N, 15.4
Found: C, 46.16; H, 3.41; N, 15.45.

High-Pressure Liquid Chromatography--One peak representing 100% of the total peak areas was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254
- Average retention time: 521 sec 2,5-dinitrotoluene 100%.

Gas Chromatography--One major component (representing 99.98% of the total peak areas) and one minor component were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 718 sec 2,5-dinitrotoluene 99.98%; 664 sec impurity 0.02%.



SPECTRUM NO. 5	ORIGIN	LEGEND A: Aromatic C-H stretch	REMARKS SLOW
SAMPLE 2,5-DINITROTOLUENE (KBr PELLET)		1 B: N=O stretch asymmetric	SLIT = 1
		~~C: N=O stretch symmetric~~	F: C=C ring stretch
	PURITY	D: In plane C-H bend	G: CH_3-C-H stretch
I.D.: K & K LABS		2. E: Out-of-plane C-H bend	H: Ar-NO_2 C-N stretch
LOT 21502-A	PHASE	DATE MAY 10, 1977	
	THICKNESS	OPERATOR INGERSOLL	

SPECTRUM NO. 13
SAMPLE

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK

FIGURE 49 INFRARED SPECTRUM OF 2,5-DINITROTOLUENE

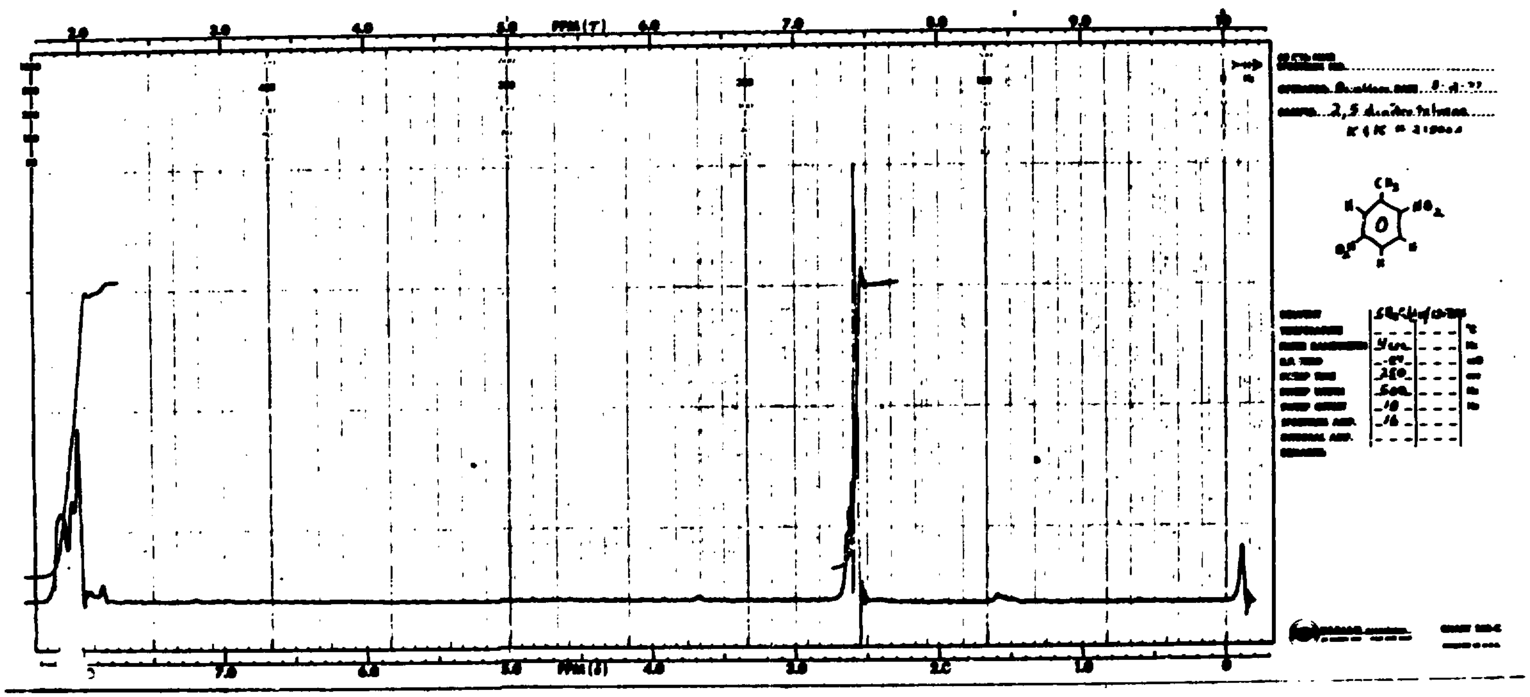


FIGURE 50 NMR SPECTRUM OF 2,5-DINITROTOLUENE

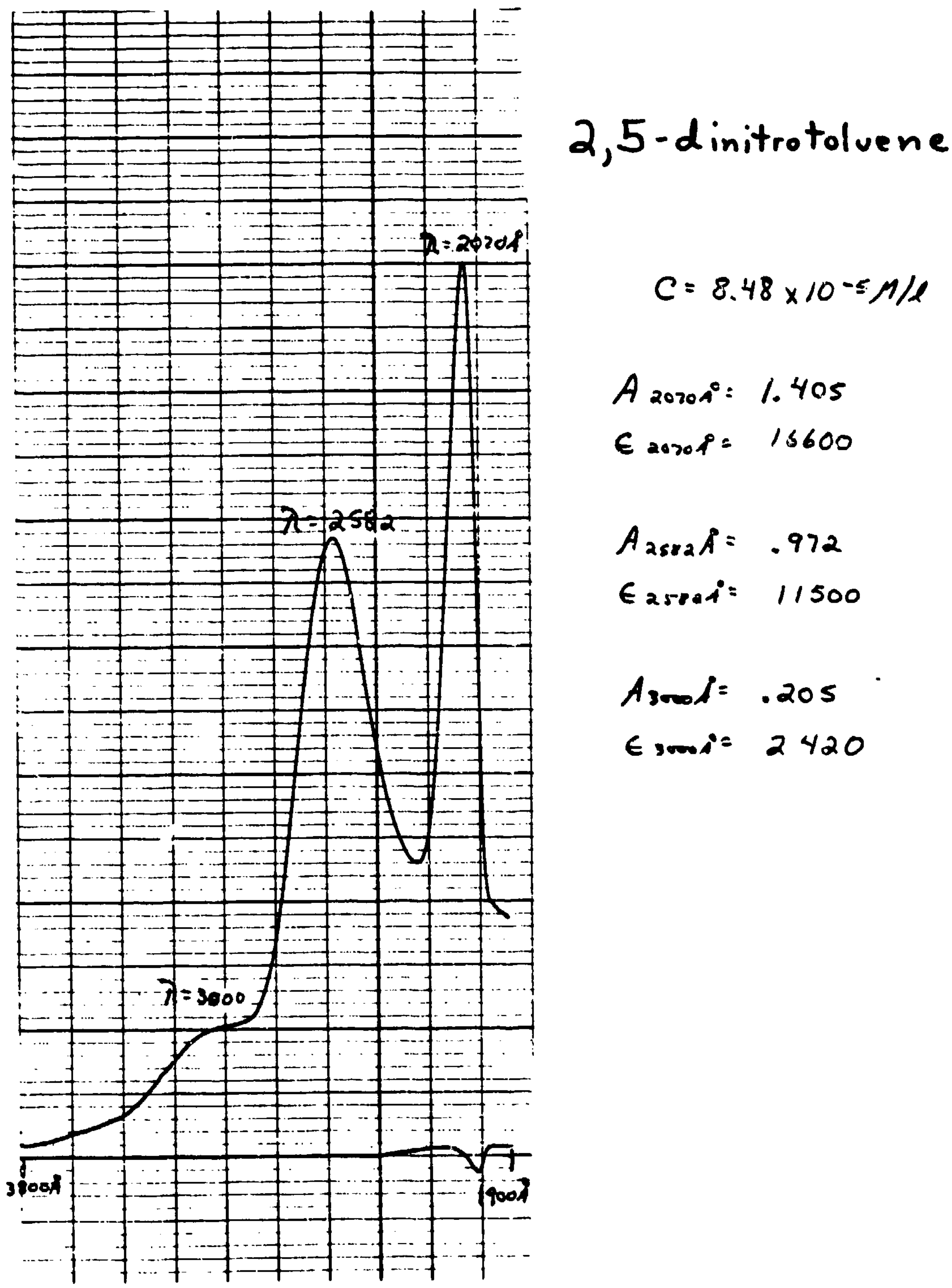


FIGURE 51 UV SPECTRUM OF 2,5-DINITROTOLUENE

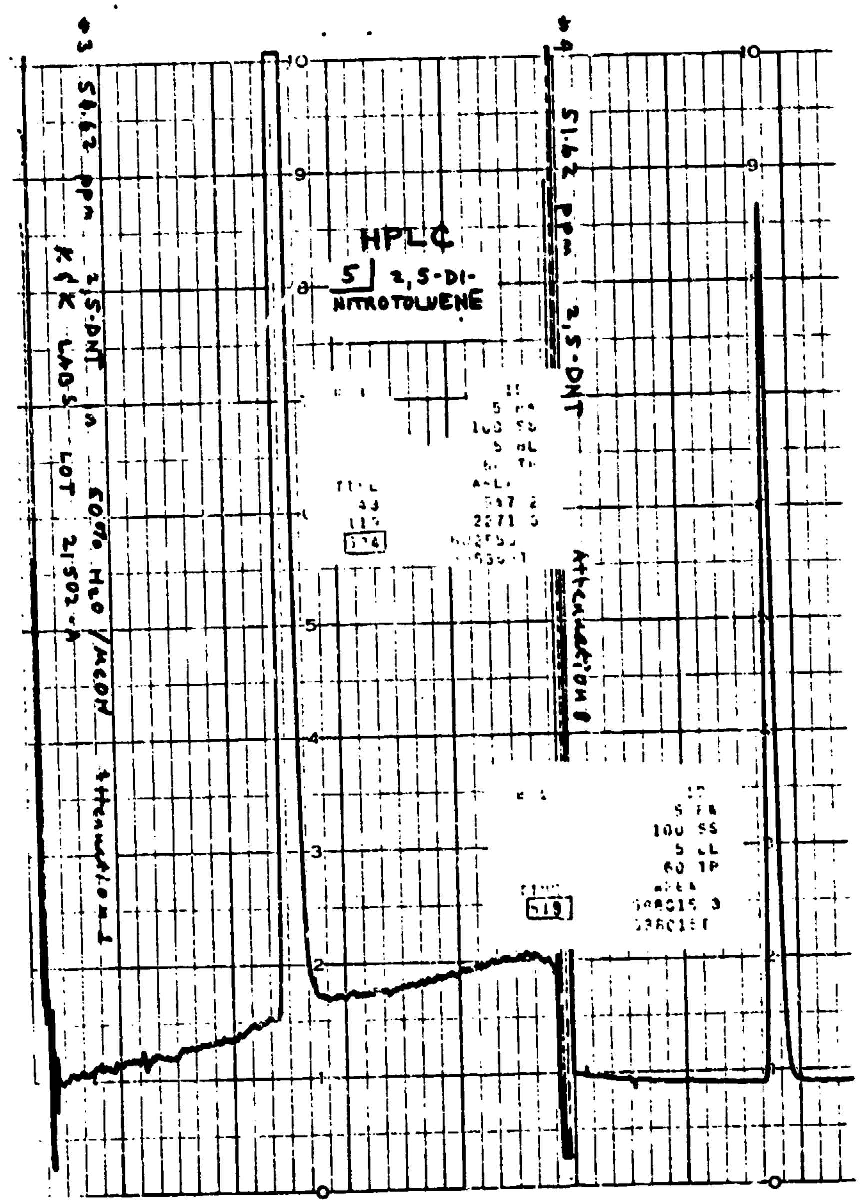
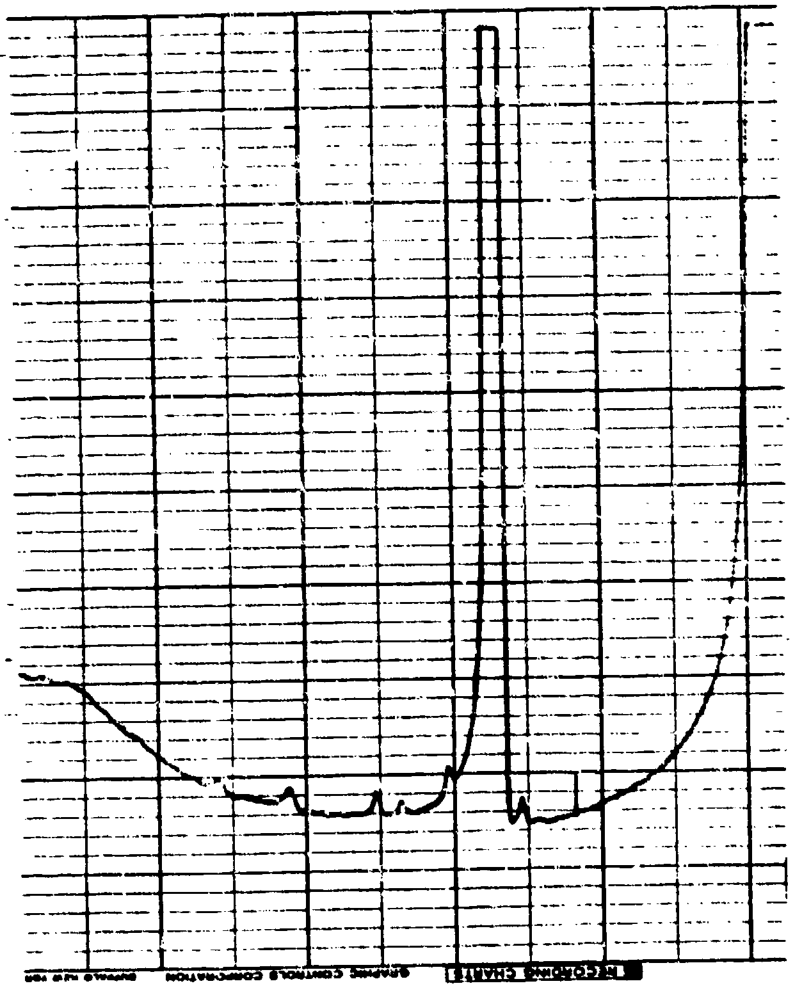


FIGURE 52 HPLC CHROMATOGRAM OF 2,5-DINITROTOLUENE

GC
2,5 Dinitrotoluene



25	6940534
26	1922351
529	
664	320
718	1392750
1015	203
2805	3
2815	1
	10256150

Donaldson 3-24-77
[redacted]
DC 200 ... 80/100 ... 100-220°
5 ... 220 °C
N_2 ... 200 °C
20 ... 2ul
10^{-10}, Atten 1 ... 16°/min
Sample: 2,5 DNT ... 4

FIGURE 53 GC SPECTRUM OF 2,5-DINITROTOLUENE

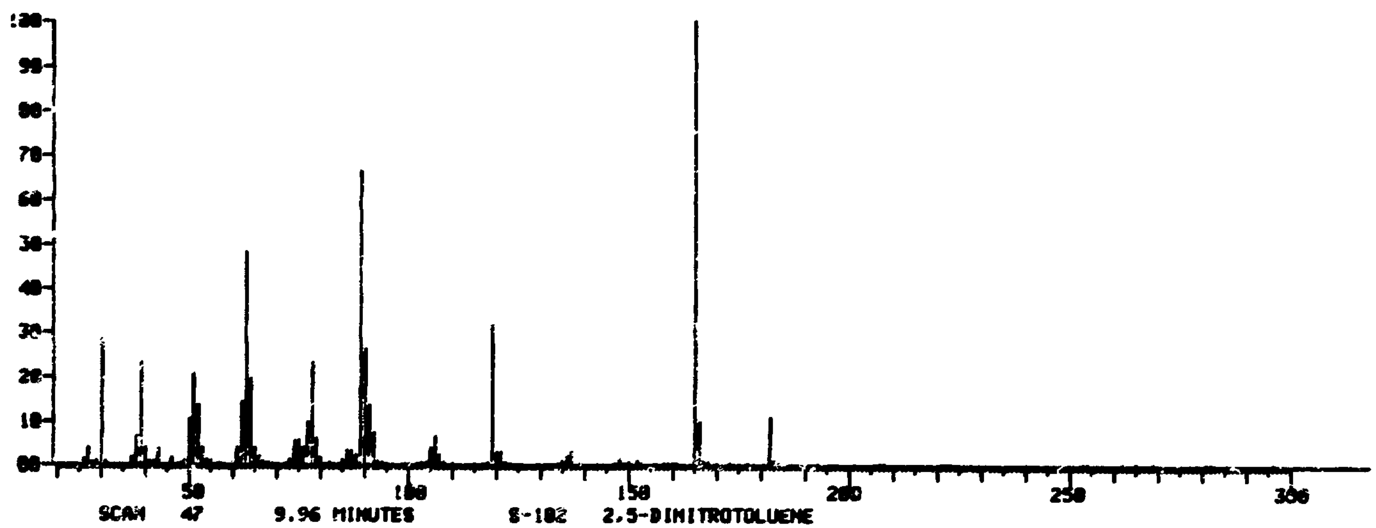
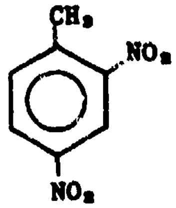


FIGURE 54 MASS SPECTRUM OF 2,5-DINITROTOLUENE

4.9 **2,4-Dinitrotoluene**

1-Methyl-2,4-dinitrobenzene

[121-14-2]



Source: ICN
Lot No. 54823
Catalog No. 5758

Identity

Ir—The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference #175 for 2,4-dinitrotoluene (KBr pellet). The following bands were observed:

(1) KBr pellet 3.25 (=C-H, aromatic), 3.5 (C-H, methyl), 6.2, 6.9 (C=C, ring), 6.5, 7.4 (N=O), 9.38, 9.7, 13.6 (C-H), 11.8 (C-N, aromatic NO_2), 7.9, 8.3, 8.7, 8.8, 10.2, 10.95, 12.6, 13.05, 14.15 μm.

(2) (Thin film in $CHCl_3$) 5-6 (aromatic overtones—1,2,4-benzenoid substitution) μm.

Nmr—The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.78 (singlet, 3H) CH_3; δ 7.67 (doublet, H, J = 9 cps) H_a

δ 8.38 (quartet, H; J_{b-a} = 9, J_{b-c} = 2.5) H_b

δ 8.73 (doublet, H, J = 2.5) H_c.

uv (Methanol)—λ_{max} = 207.0 nm, A = 0.624, ε = 11,100

λ_{max} = 240.0 nm, A = 0.809, ε = 14,300.

Purity

Elemental Analysis—

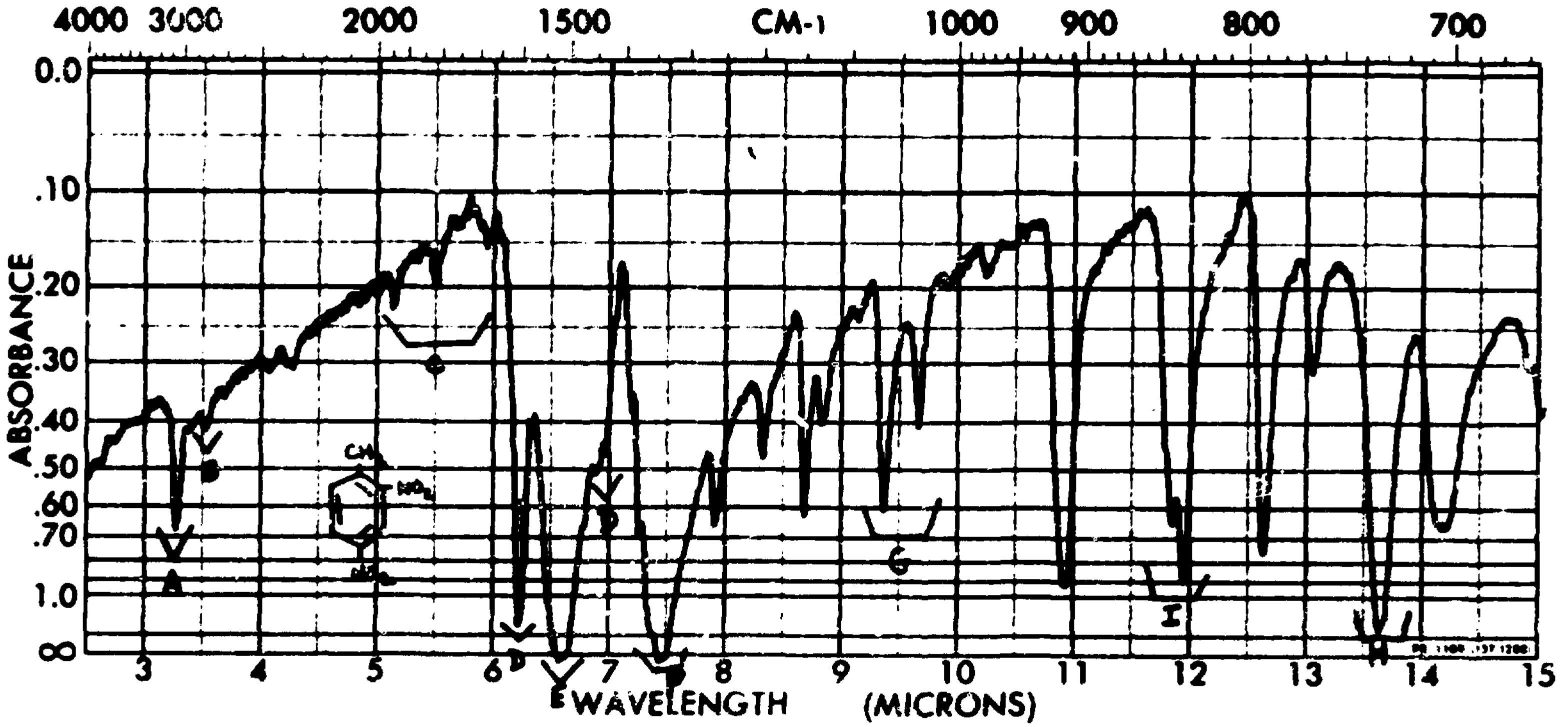
Anal. for $C_7H_6N_2O_4$: **Calcd:** C, 46.2; H, 3.3; N, 15.4
Found: C, 46.21; H, 3.37; N, 15.43.

High-Pressure Liquid Chromatography--One major component (representing 99.5% of the total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Retention time: 591 sec 2,4-dinitrotoluene 99.5%; 545 sec impurity 0.5%.

Gas Chromatography--One major component (representing 98.3% of the total peak areas) and two minor components were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 787 sec 2,4-dinitrotoluene 98.3%; 673 sec impurity 1.4%; 734 sec impurity 0.3%.



SPECTRUM NO. 6	ORIGIN	LEGEND A: Aromatic C-H stretch. 1. B: Methyl C-H stretch C: Overtones 2. D: C=C ring stretch	REMARKS Slow SLIT = 1
SAMPLE 2,4-DINITROTOLUENE (KBr PELLET)	PURITY		E: N=O stretch asymmetric F: N=O stretch symmetric G: In plane C-H bend. H: Out-of-plane C-H bend I: Ar-NO₂ C-N stretch
I.D. Maltz 600 g	PHASE	DATE MAY 9, 1977	
	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO. 15
SAMPLE

RECORDING CHARTS

FIGURE 55 INFRARED SPECTRUM OF 2,4-DINITROTOLUENE

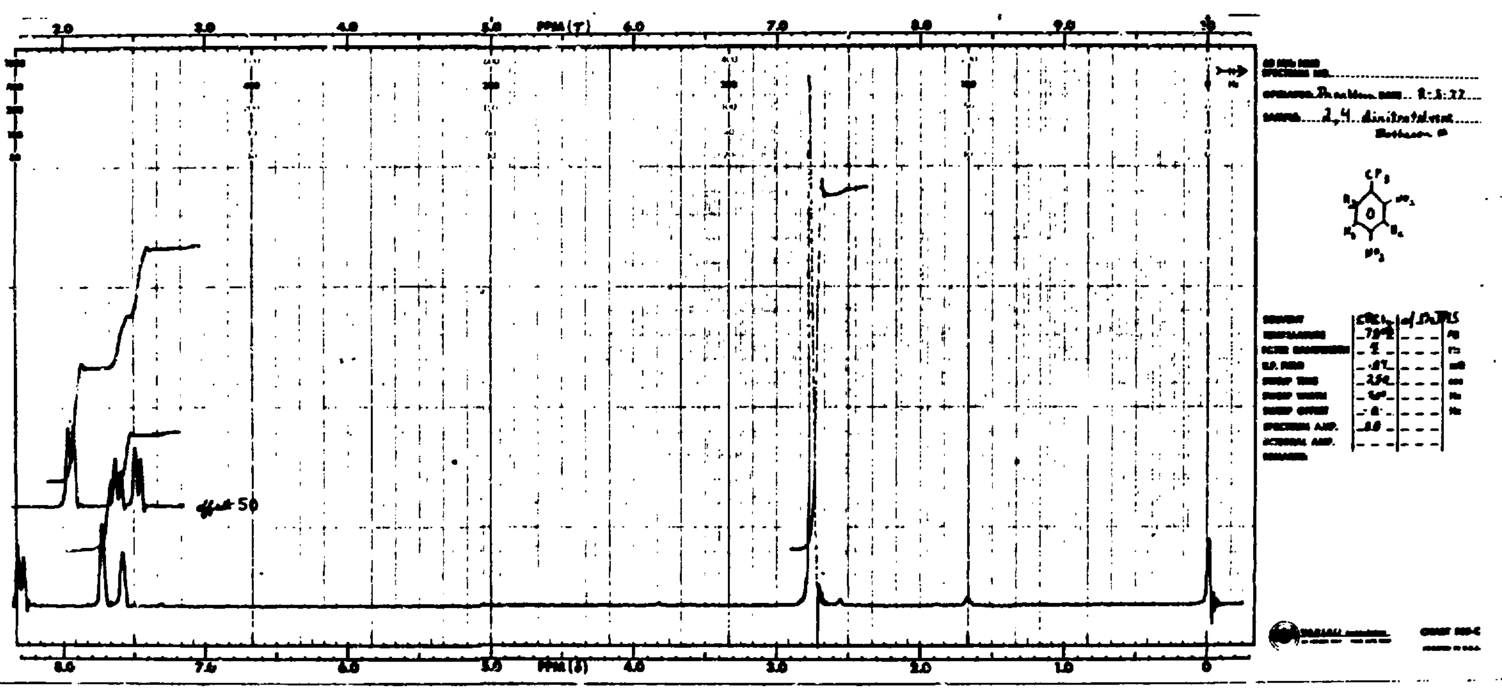


FIGURE 56 NMR SPECTRUM OF 2,4-DINITROTOLUENE

2,4-dinitrotoluene

$C = 5.64 \times 10^{-5}\ M/l$

$A_{2070\text{Å}} = .624$

$\epsilon_{2070\text{Å}} = 11100$

$A_{2400\text{Å}} = .809$

$\epsilon_{2400\text{Å}} = 14300$

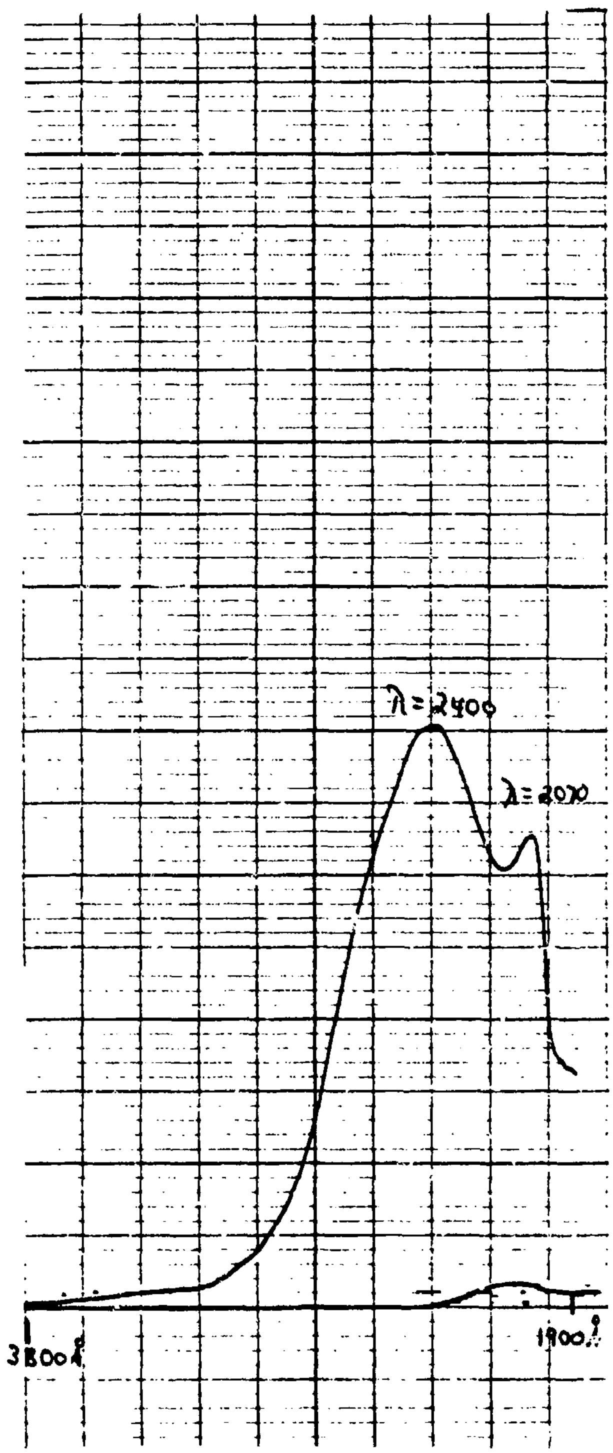


FIGURE 57 UV SPECTRUM OF 2,4-DINITROTOLUENE

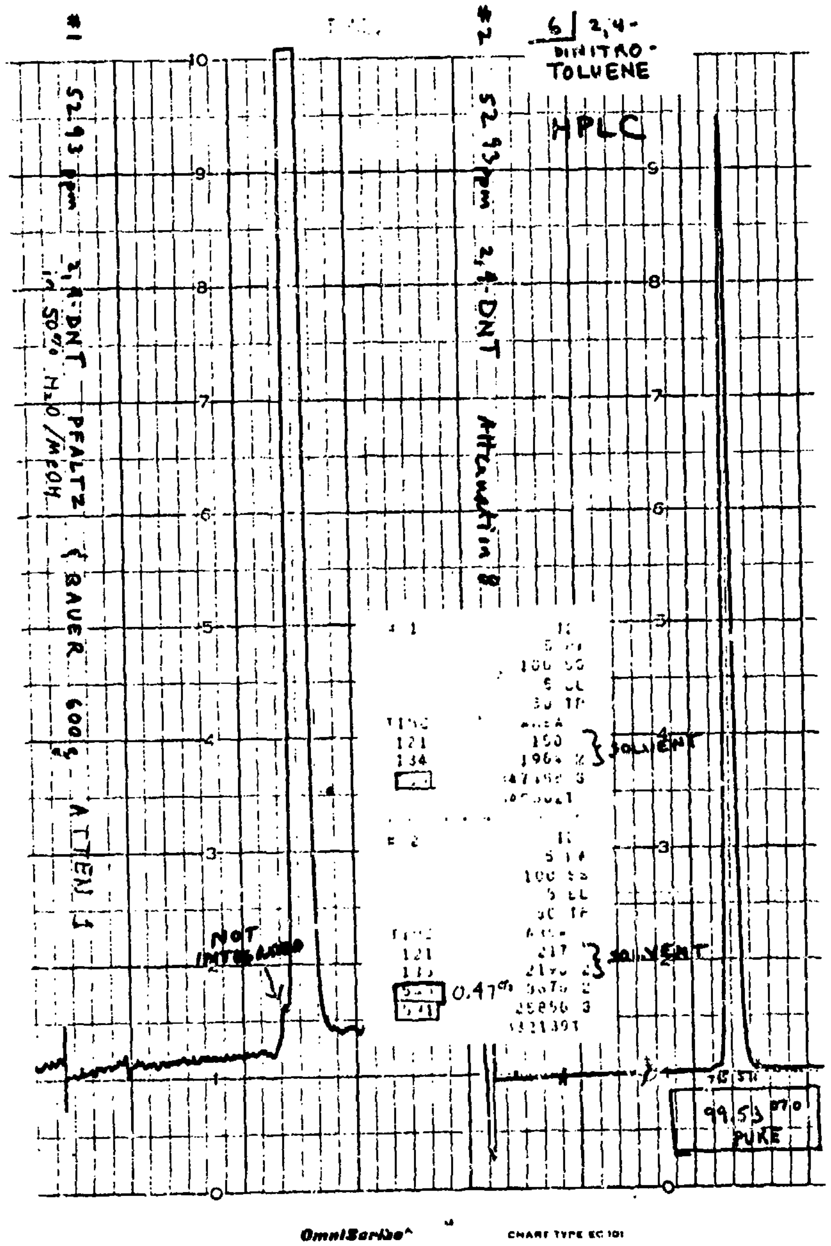
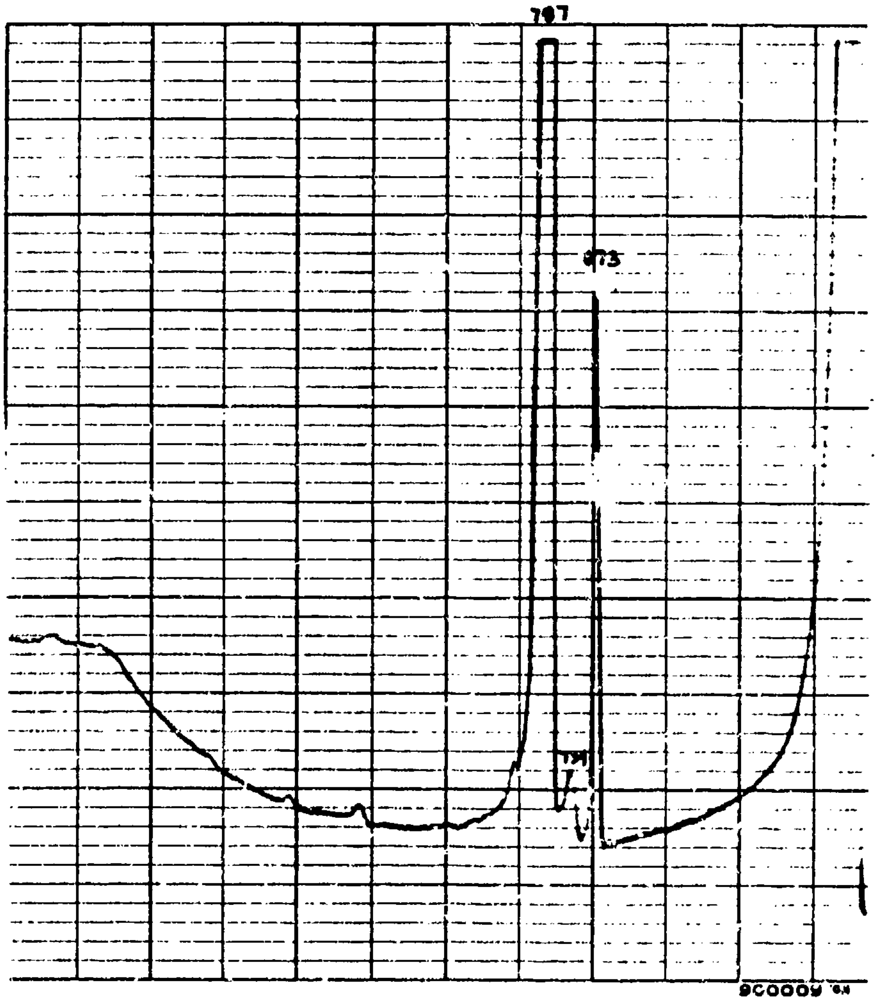


FIGURE 58 HPLC CHROMATOGRAM OF 2,4-DINITROTOLUENE

GC

2,4 Dinitrotoluene



25 8642473

673 9666

734 2380

$\boxed{787}$ 661621

2120

9336140

Operator [illegible] Date 3-24-77

Column: [redacted]
10% DC 200 ... 80/100

Length 5 ft.

Carrier Gas N_2

Rate 20 ml/min.

Sensitivity 10^{-8}, Atten 1

Sample 2,4 DNT

Temperatures:

Column 80-220°C

Detector 220 °C

Sampling 250 °C

Sample Size 2ul

Chart Speed 16 in/min

Temp. Rate 4 °/min.

FIGURE 59 GC SPECTRUM OF 2,4-DINITROTOLUENE

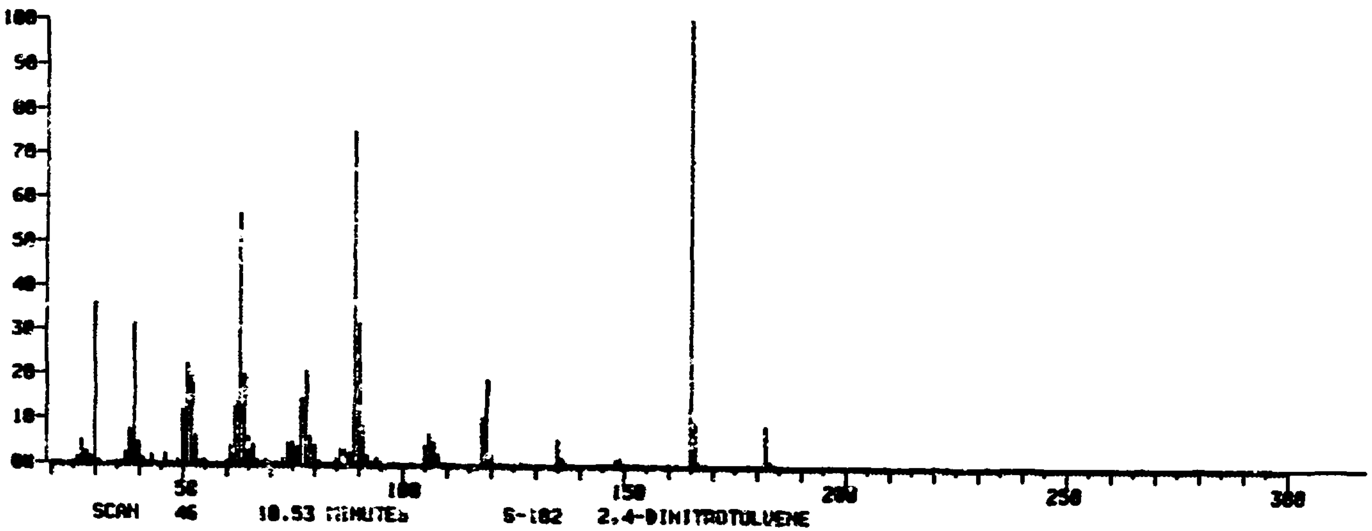
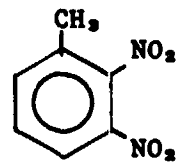
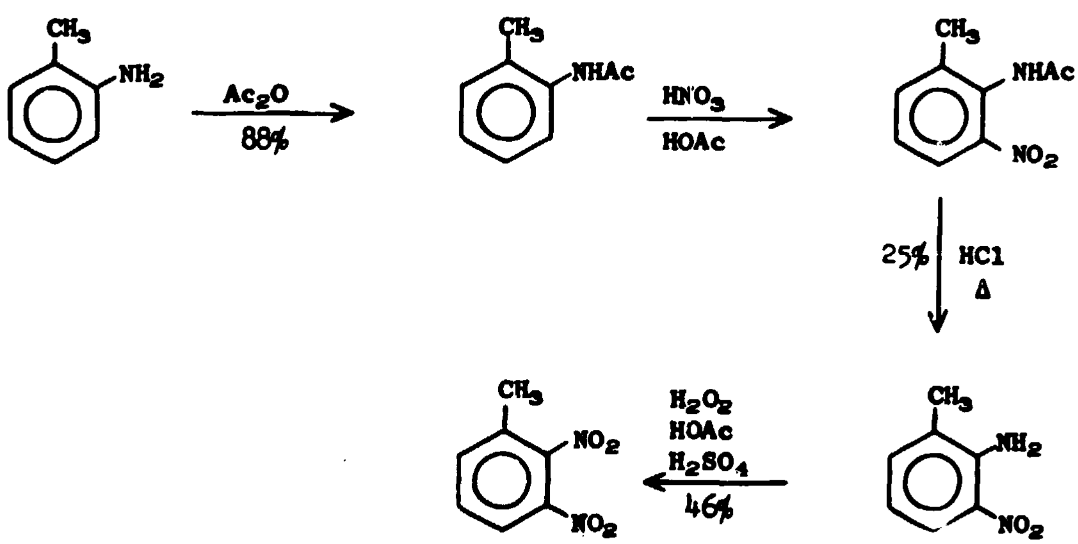


FIGURE 60 MASS SPECTRUM OF 2,4-DINITROTOLUENE

4.10 <u>2,3-Dinitrotoluene</u>
1-Methyl-2,3-dinitrobenzene
[602-01-7]



Source: Synthesis, SRI



<u>Identity</u>

<u>Ir</u>--The ir spectrum was consistent with the proposed structure. The following bands were observed:

(1) (KBr pellet) 3.3 (=C-H, aromatic), 3.5 (C-H, methyl), 6.2, 6.9 (C=C, ring), 6.5, 7.45 (N=O), 9.3, 9.55 (C-H), 11.7 (C-N, aromatic NO_2), 7.3, 8.4, 8.54, 10.8, 12.35, 13.45, 14.2 μm.

(2) (Thin film in $CHCl_3$) 5-6 (aromatic overtones--not pure 1,2,3-benzenoid substitution) μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.45 (singlet, 3H) CH_3; δ 7.65 (multiplet, 2H) $H_{a \& a'}$
δ 8.03 (quartet, H, $J_{b-a'} = 7$ cps, $J_{b-a} = 3.5$ cps) H_b.

uv (Methanol)--λ_{max} = 206.5 nm, A = 0.933, ε = 16,000
λ_{max} = 254.0 nm, A = 0.362, ε = 6220.

Purity (100%)

Elemental Analysis--

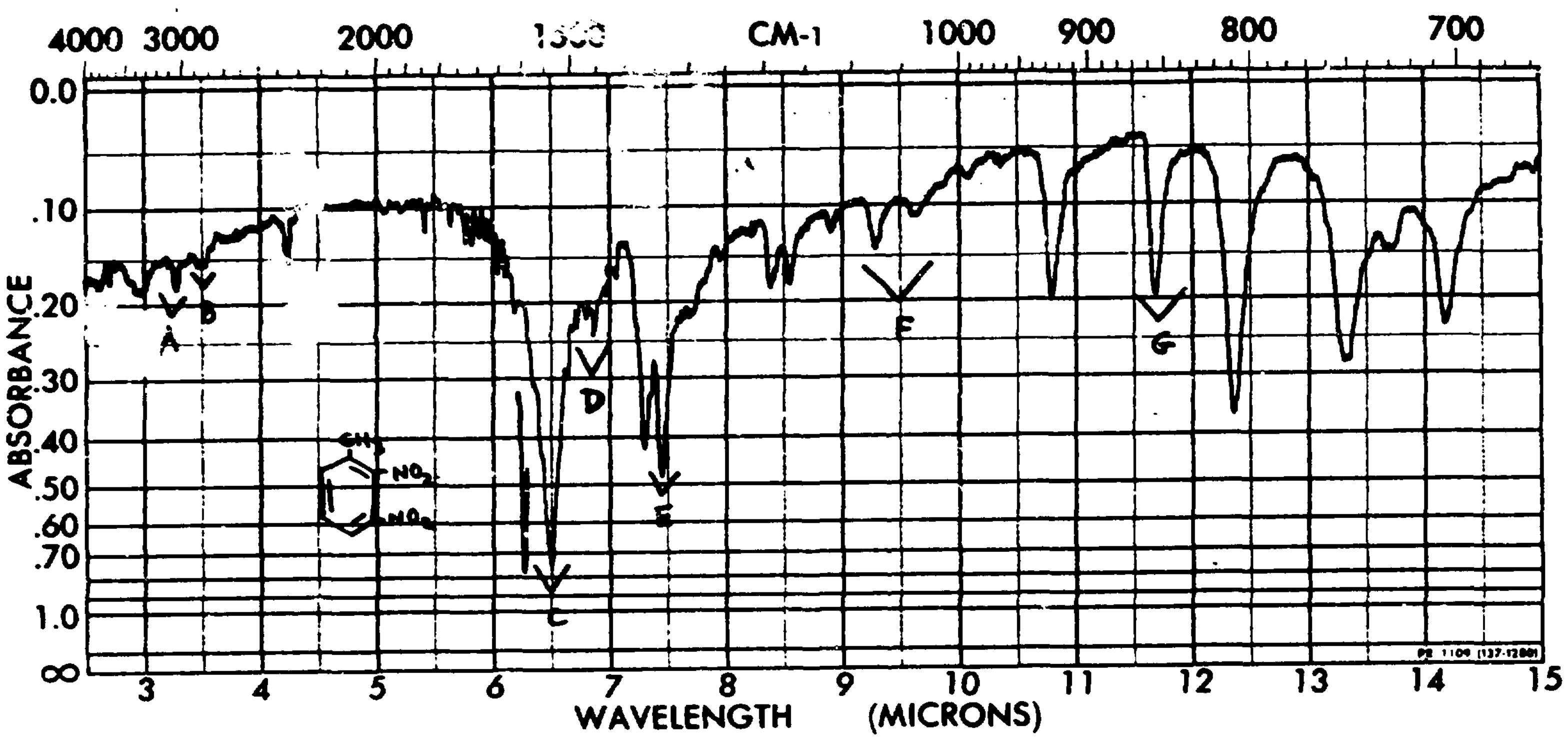
Anal. for $C_7H_6N_2O_4$: Calcd: C, 46.2; H, 3.3; N, 15.4
Found: C, 46.13; H, 3.38; N, 15.35.

High-Pressure Liquid Chromatography--One peak representing 100% of the total peak areas was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 589 sec 2,3-dinitrotoluene 100%.

Gas Chromatography--One peak (representing 100% of the total peak areas) was observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 200°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 756 sec 2,3-dinitrotoluene 100%.



SPECTRUM NO. 18
SAMPLE

SPECTRUM NO. 7	ORIGIN	LEGEND A: Aromatic C-H stretch. B: Methyl C-H stretch 1. C: N=O stretch asymmetric D: C=C ring stretch. 2. E. N=O stretch symmetric	REMARKS SLOW SLIT = 1 F: Inplane C-H bend G: Ar-NO_2 C-N stretch.
SAMPLE 2,3-DINITROTOLUENE (KBr PELLET)	PURITY		
I.D.: ALDRICH LOT NO. 051647	PHASE	DATE MAY 11, 1977	
LOT 14,756-7	THICKNESS	OPERATOR C. INGERSOLL	

FIGURE 61 INFRARED SPECTRUM OF 2,3-DINITROTOLUENE

RECORDING CHARTS GRAPHIC CONTROLS CORPORATION

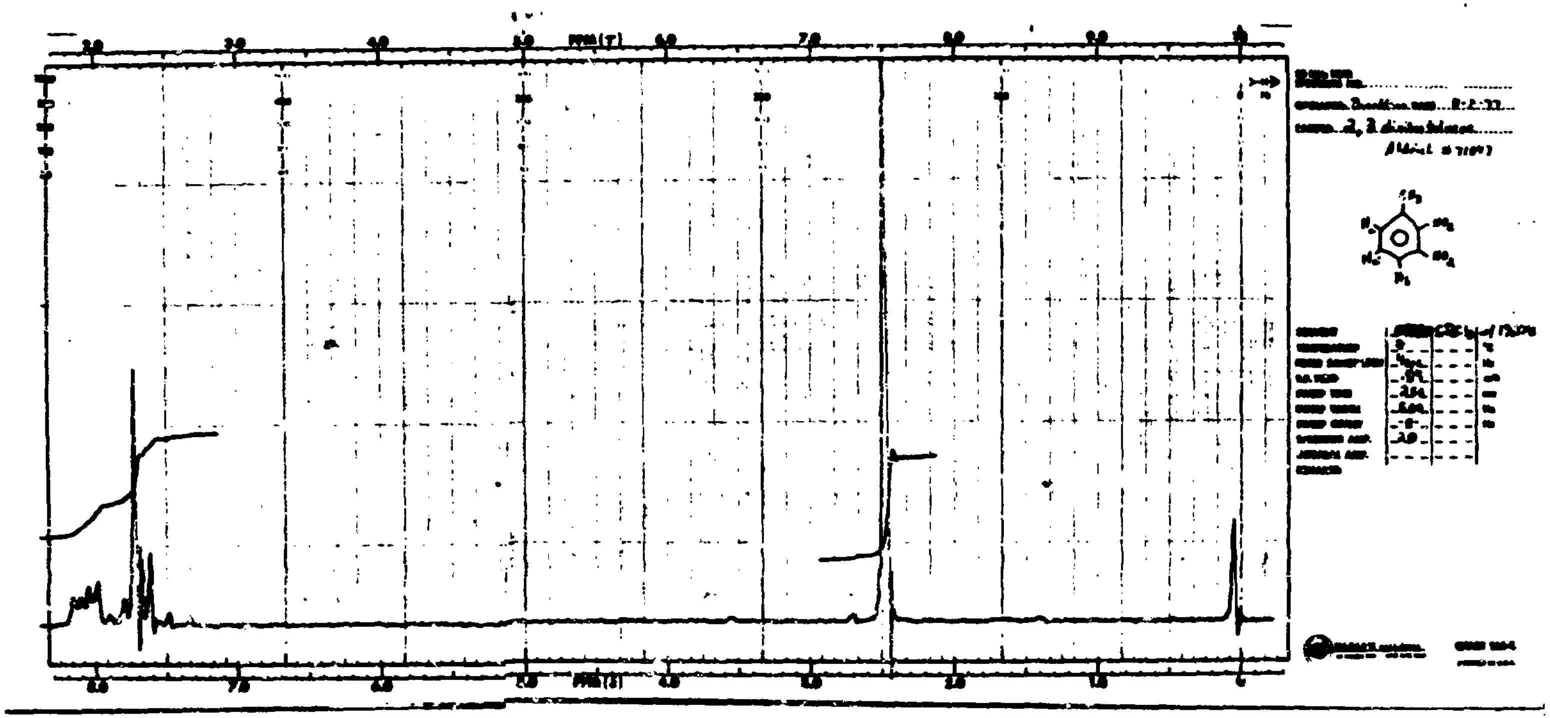
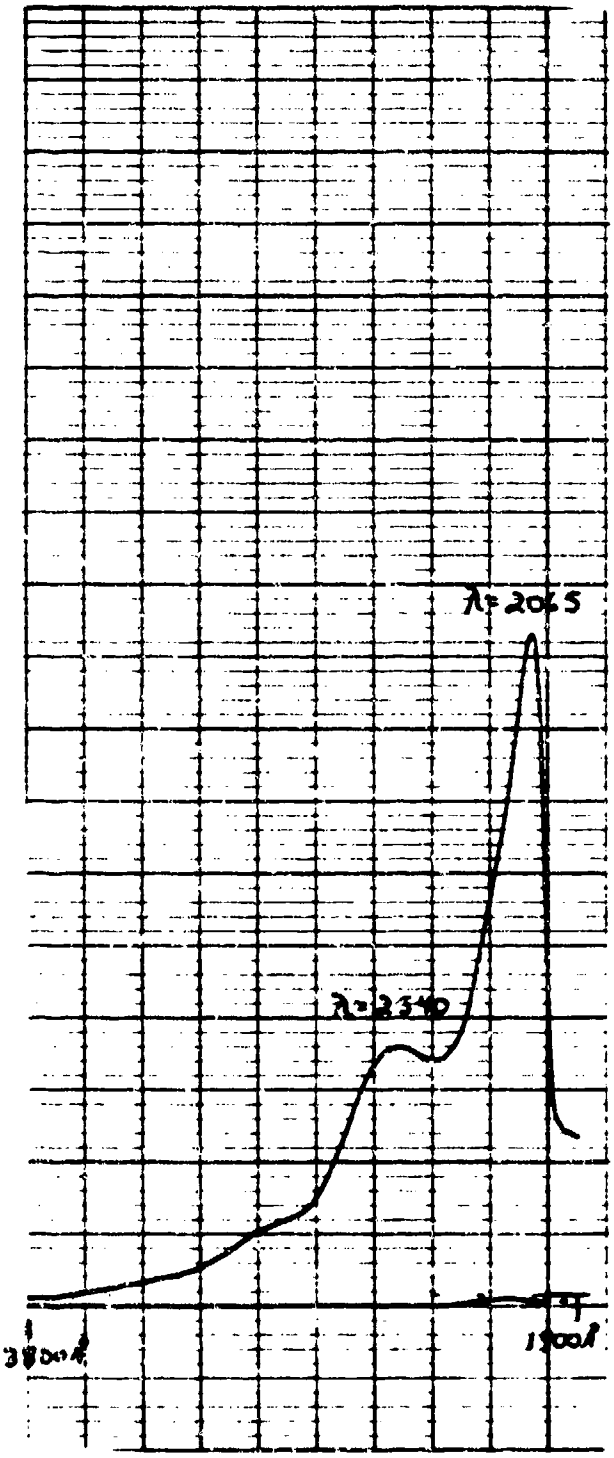


FIGURE 62 NMR SPECTRUM OF 2,3-DINITROTOLUENE



2, 3-dinitrotoluene

$C = 5.82 \times 10^{-5}\ M/l$

$A_{2065\,Å} = .933$

$\epsilon_{2065\,Å} = 16000$

$A_{2340\,Å} = .362$

$\epsilon_{2340\,Å} = 6220$

FIGURE 63 UV SPECTRUM OF 2,3-DINITROTOLUENE

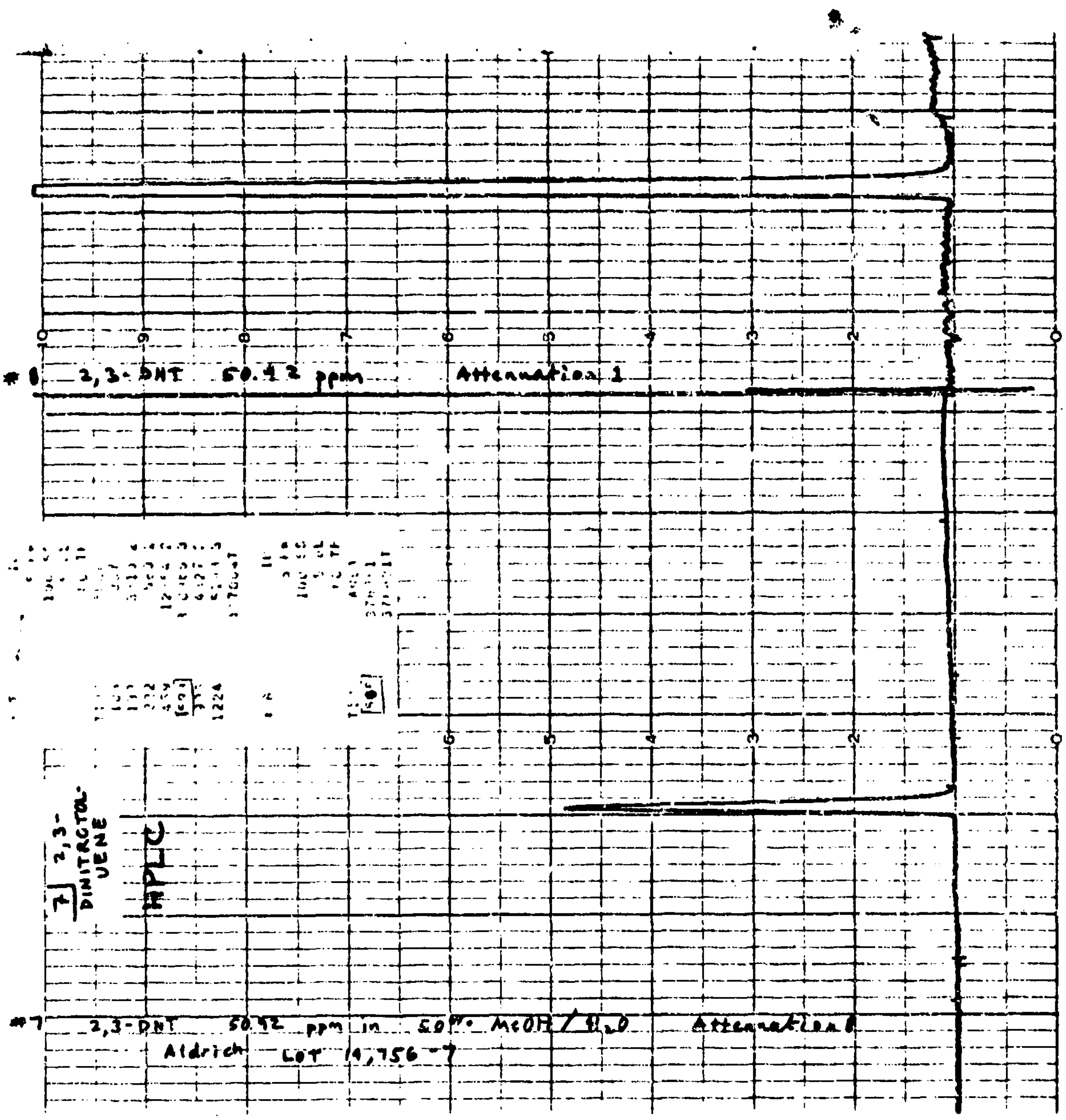
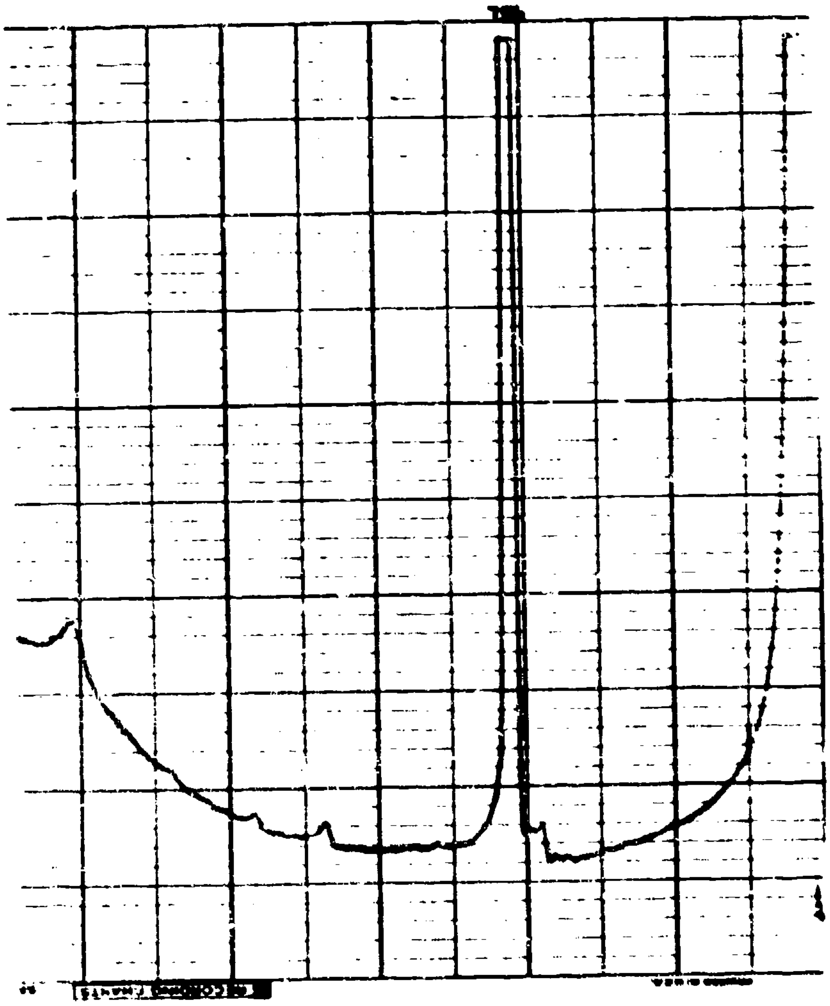


FIGURE 64 HPLC CHROMATOGRAM OF 2,3-DINITROTOLUENE

2,3 Dinitrotoluene



26	5957627
756	179732
1825	3069
	6141310

Operator Dewnhdoer Date 3-24-77

Column [redacted] Temperatures:
.05 DC 200 ... Column 220 °C
Length 5 ft.
Detector 220 °C
Carrier Gas N_2
Sampler 206 °C
Rate 20 ml/min.
Sample Size 2 µl
Sensitivity 10^{-}
Chart Speed 1 in/min
Sample 2,3-DNT
Temp. Rate 4 °/min.

FIGURE 65 GC SPECTRUM OF 2,3-DINITROTOLUENE

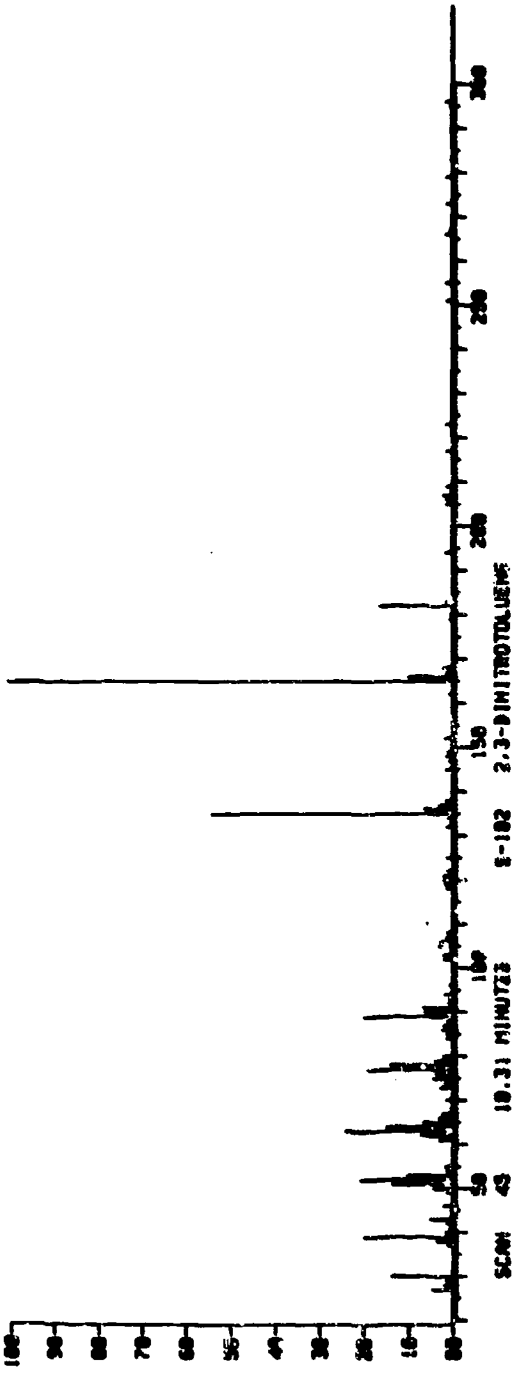
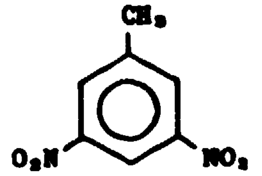
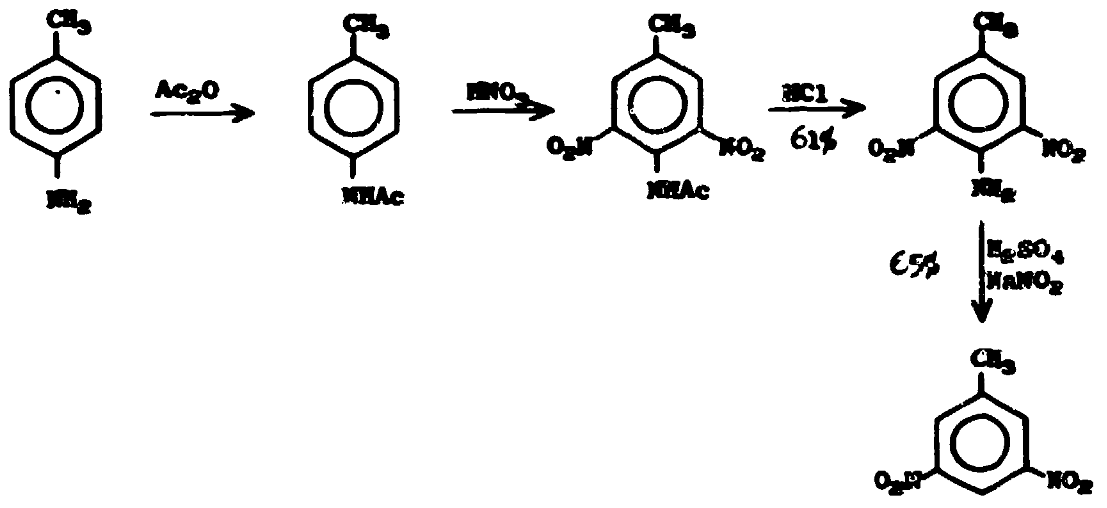


FIGURE 66 MASS SPECTRUM OF 2,3-DINITROTOLUENE

4.11 <u>3,5-Dinitrotoluene</u>
1-Methyl-3,5-dinitrobenzene
[618-85-9]



Source: Synthesis, SRI



<u>Identity</u>

<u>Ir</u>—The ir spectrum was consistent with the proposed structure. The following bands were observed:

(1) (KBr pellet) 3.25 (=C-H, aromatic), 3.5 (C-H, methyl), 6.25, 6.85 (C=C, ring), 6.5, 7.4 (N=O), 9.55, 13.65 (C-H), 8.9, 9.3, 10.5, 10.9, 11.05, 11.1, 12.4, 13.1 μm.

(2) Br pellet) 5-6 (aromatic overtones—possibly 1,3,5-benzenoid substitution) μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.69 (singlet, 3H) CH_3; δ 8.41 (singlet, 2H) H_a;
δ 8.81 (singlet, H) H_b.

uv (Methanol)--λ_{max} = 203.0 nm, A = 0.605, ε = 9530
λ_{max} = 239.4 nm, A = 1.113, ε = 17,500
λ_{max} = 300.0 nm, A = 0.104, ε = 1640.

Purity (100%)

Elemental Analysis--

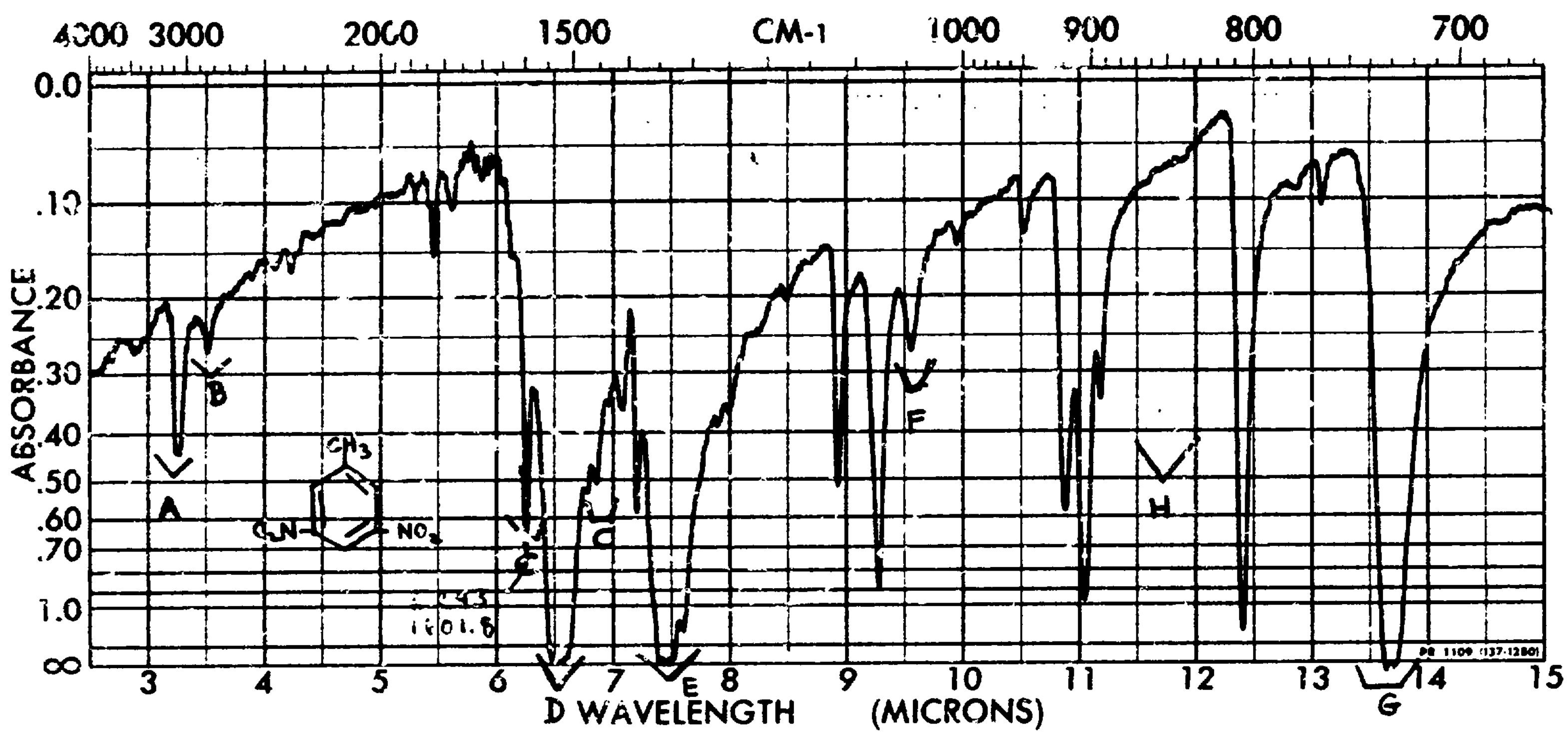
Anal. for $C_7H_6N_2O_4$: Calcd: C, 46.2; H, 3.3; N, 15.4
Found: C, 46.33; H, 3.37; N, 15.25.

High-Pressure Liquid Chromatography--One peak representing 100% of the total peak areas was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 589 sec 3,5-dinitrotoluene 100%.

Gas Chromatography--One peak (representing 100% of the total areas) was obtained by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 789 sec 3,5-dinitrotoluene 100%.



SPECTRUM NO. 20
SAMPLE

SPECTRUM NO. 8	ORIGIN	LEGEND A: Aromatic C-H stretch B: Methyl C-H stretch 1 ~~C: C=C ring stretch~~ D: N=O stretch asymmetric 2 E: N=O stretch symmetric	REMARKS SLOW SLIT : 1 F: In plane C-H bend G: Out of plane C-H bend H: No Ar-NO_2 C-N stretch
SAMPLE 3,5-DINITROTOLUENE (KBr PELLET)	PURITY		
I.D. 10568-8 Wm Blucher 6-13-77	PHASE	DATE MAY 10, 1977	Less concentrated
	THICKNESS	OPERATOR INGERSOLL	

FIGURE 67 INFRARED SPECTRUM OF 3,5-DINITROTOLUENE

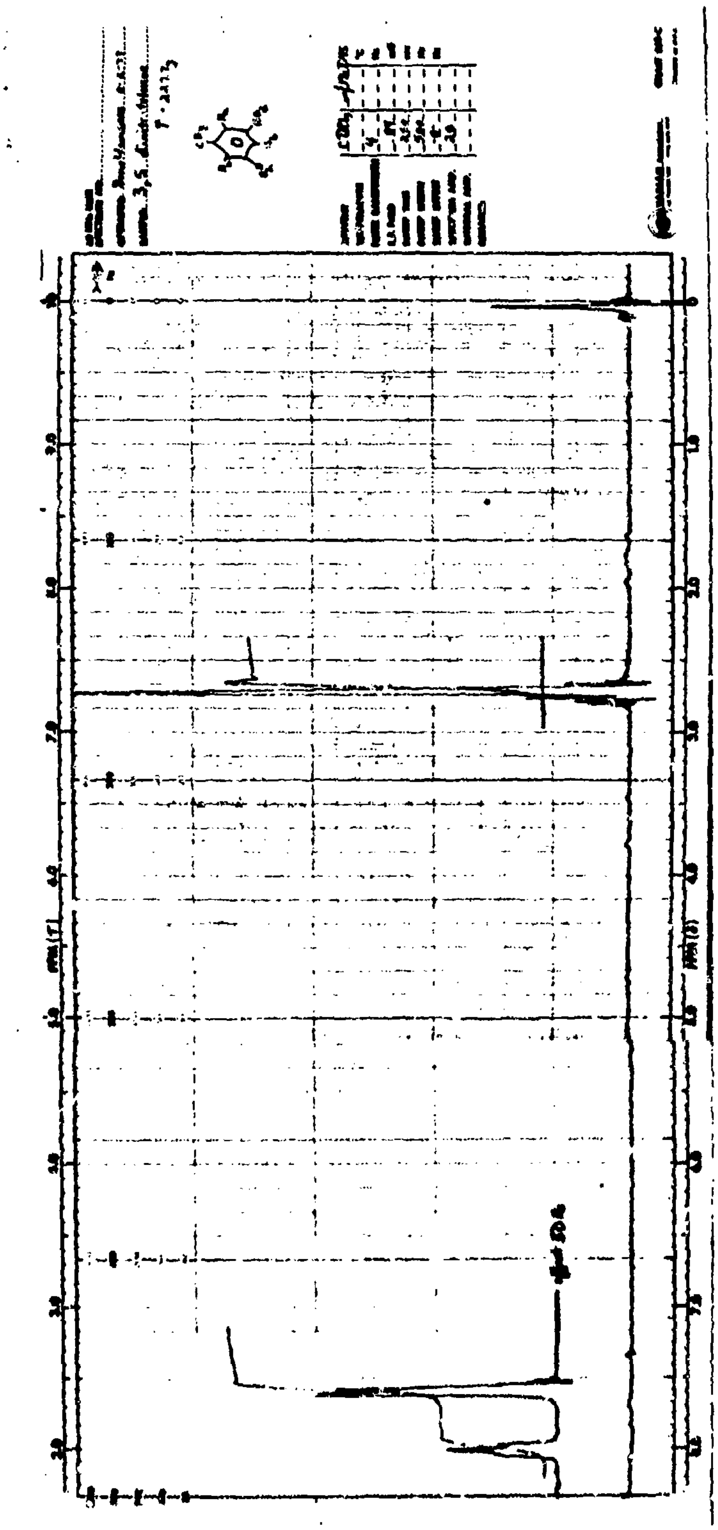
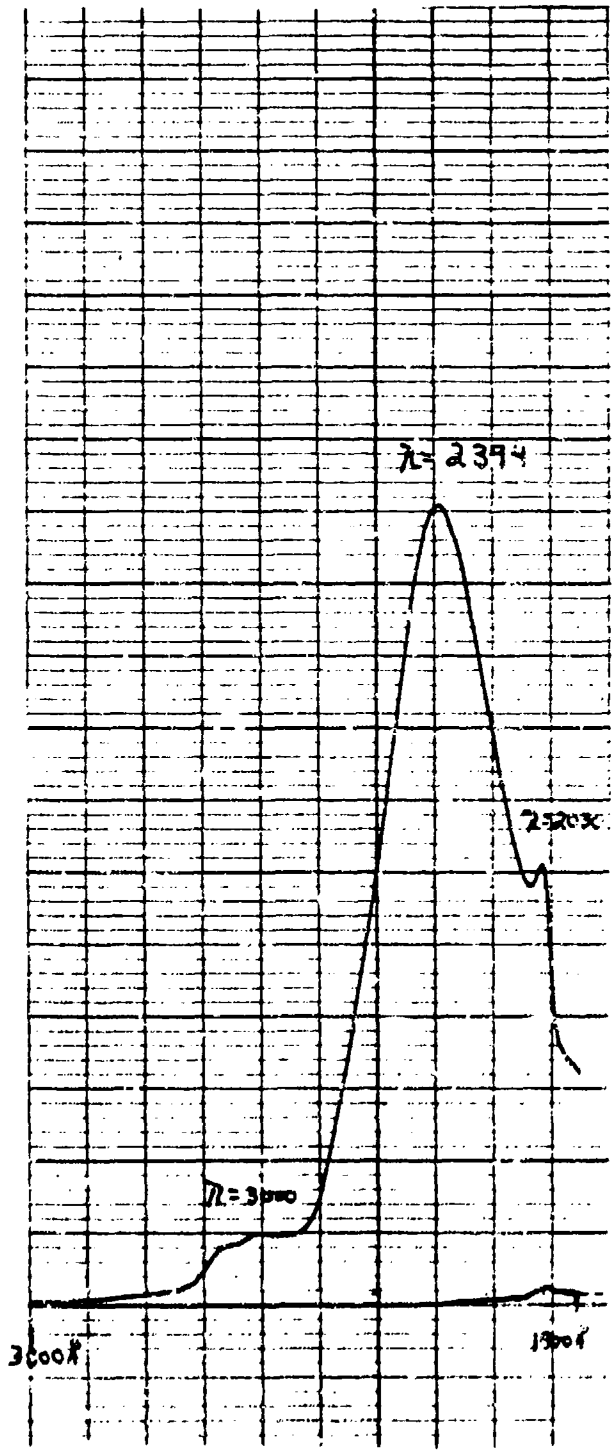


FIGURE 68 NMR SPECTRUM OF 3,5-DINITROTOLUENE



3,5-dinitrotoluene

$C = 6.35 \times 10^{-5}\ M/l$

$A_{2030Å} = .605$
$\epsilon_{2030Å} : 9530$

$A_{2394Å} = 1.113$
$\epsilon_{2394Å} = 17500$

$A_{3000Å} = .104$
$\epsilon_{3000Å} : 1640$

FIGURE 69 UV SPECTRUM OF 3,5-DINITROTOLUENE

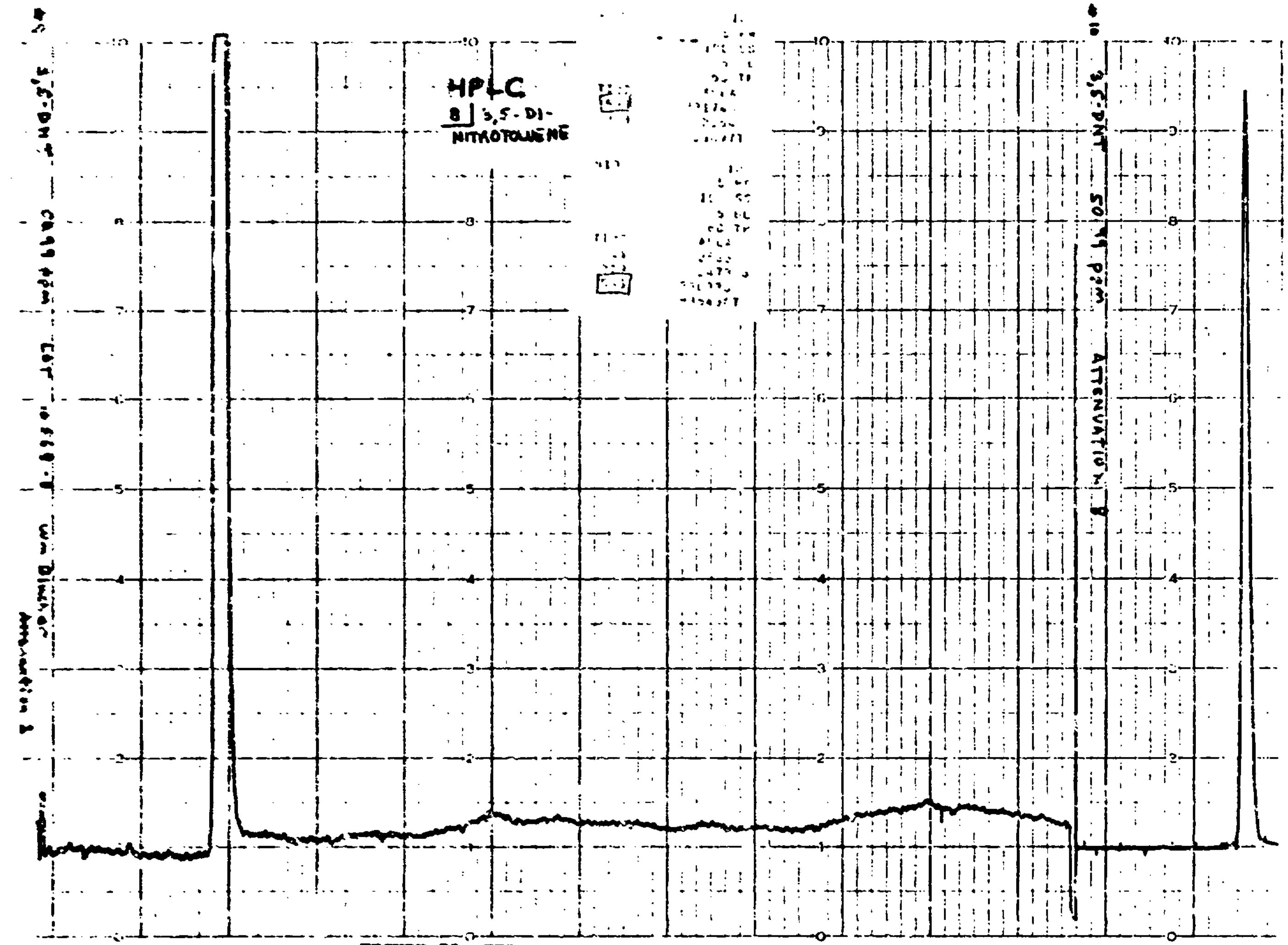
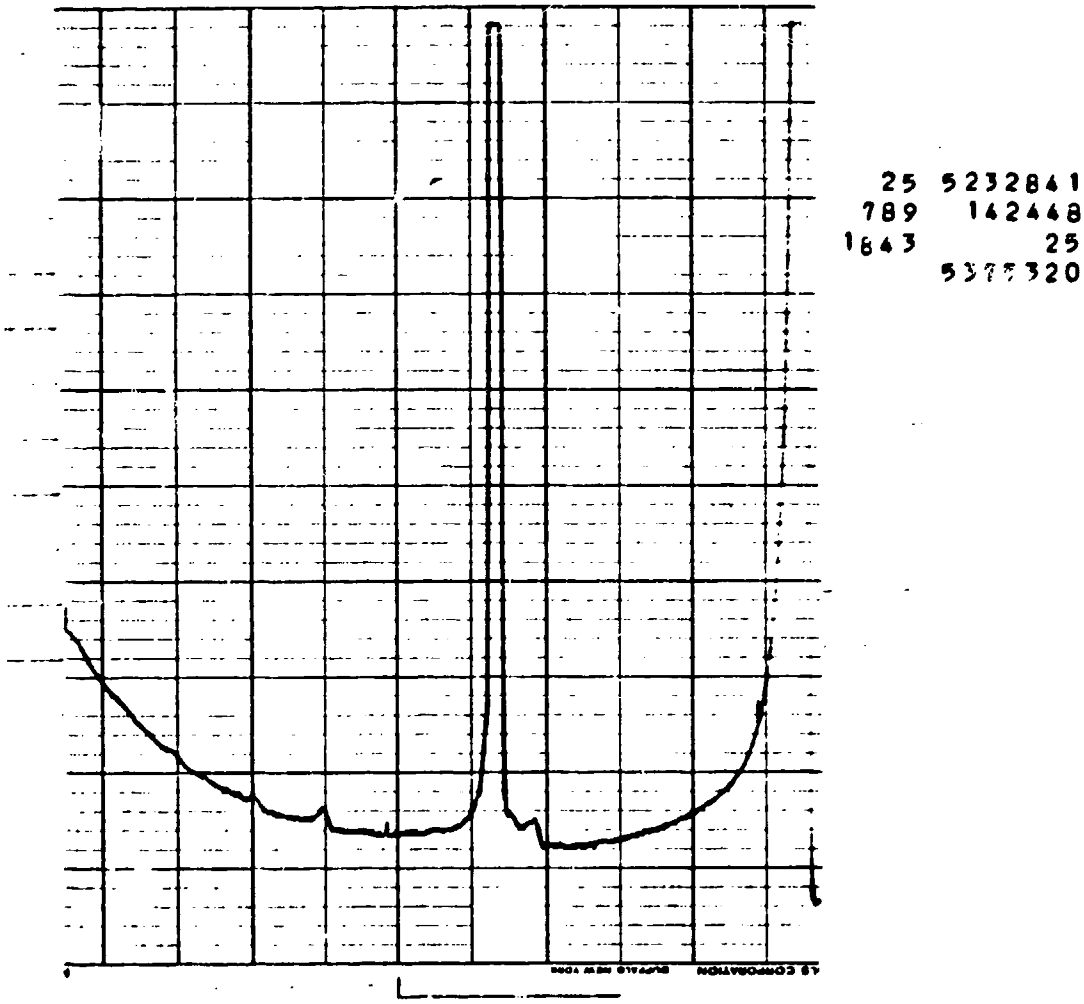


FIGURE 70 HPLC CHROMATOGRAM OF 3,5-DINITROTOLUENE

GC

3,5 Dinitrotoluene



Operator: Donaldson Date: 3-24-77

Column: [redacted] Temperatures:

10% DC [illegible] w/ HP 80/100

Length 5 ft. Column 100-220°C

Carrier Gas N_2 Detector 220 °C

Injector 200 °C

Rate 20 ml/min Sample 2µl

Sensitivity $10^{-[illegible]}$ Attn 1 Chart .16 in/min

Sample 3,5 DNT Temp Rate 4 °/min

FIGURE 71 GC SPECTRUM OF 3,5-DINITROTOLUENE

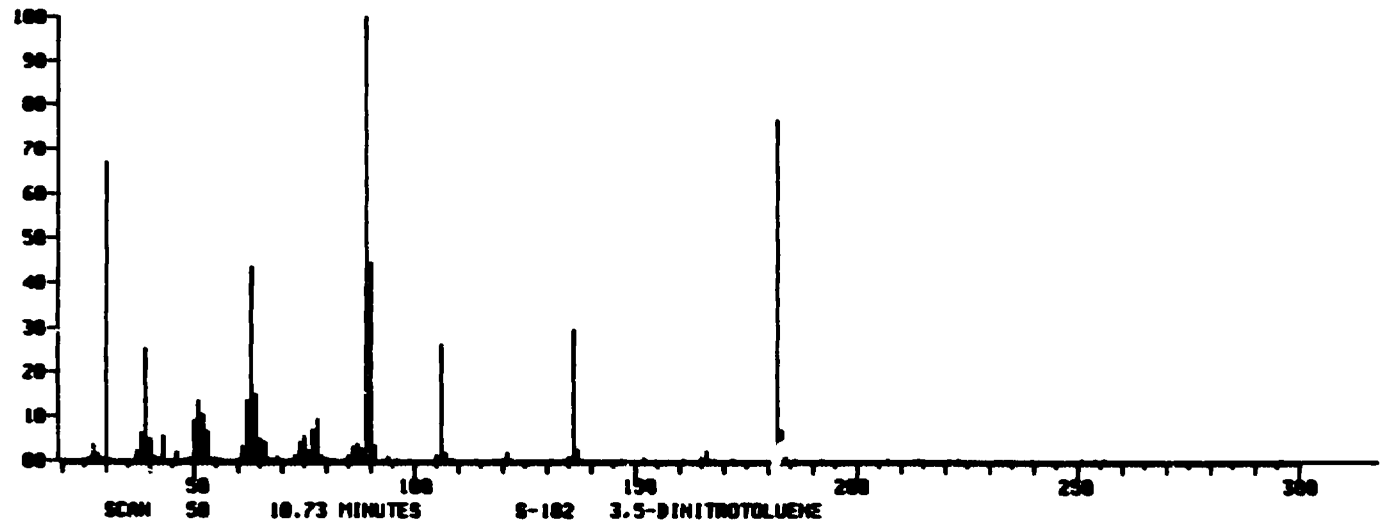
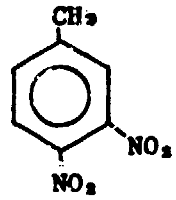


FIGURE 72 MASS SPECTRUM OF 3,5-DINITROTOLUENE

4.12 3,4-Dinitrotoluene
4-Methyl-1,2-dinitrobenzene
[610-39-9]



Source: Aldrich Chemical Company
Lot No. AB 082467
Catalog No. 14,812-1

Identity

Ir--The ir spectrum was consistent with the propored structure. The following bands were observed:

(1) (KBr pellet) 3.3 (=C-H, aromatic), 3.5 (C-H, methyl), 6.2, 6.8 (C=C, ring), 6.5, 7.4 (N=O), 9.6, 13.5 (C-H), 11.8 (C-N, aromatic NO_2), 8.2, 8.6, 8.75, 10.28, 10.8, 11.15, 12.55, 13.3, 14.55 µm.

(2) (KBr pellet) 5-6 (aromatic overtones) µm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.56 (singlet, 3H) CH_3; δ 7.65 (doublet, H_a; J = 3 cps) H;
δ 7.82 (singlet, H_b) H_b; δ 7.95 (singlet, H_c) H_c.

uv (Methanol)--λ_{max} = 217.0 nm, A = 0.910, ϵ = 13,300
λ_{max} = 260.5 nm, A = 0.421, ϵ = 6150.

Purity (99.9% ± 0.1%)

Elemental Analysis--

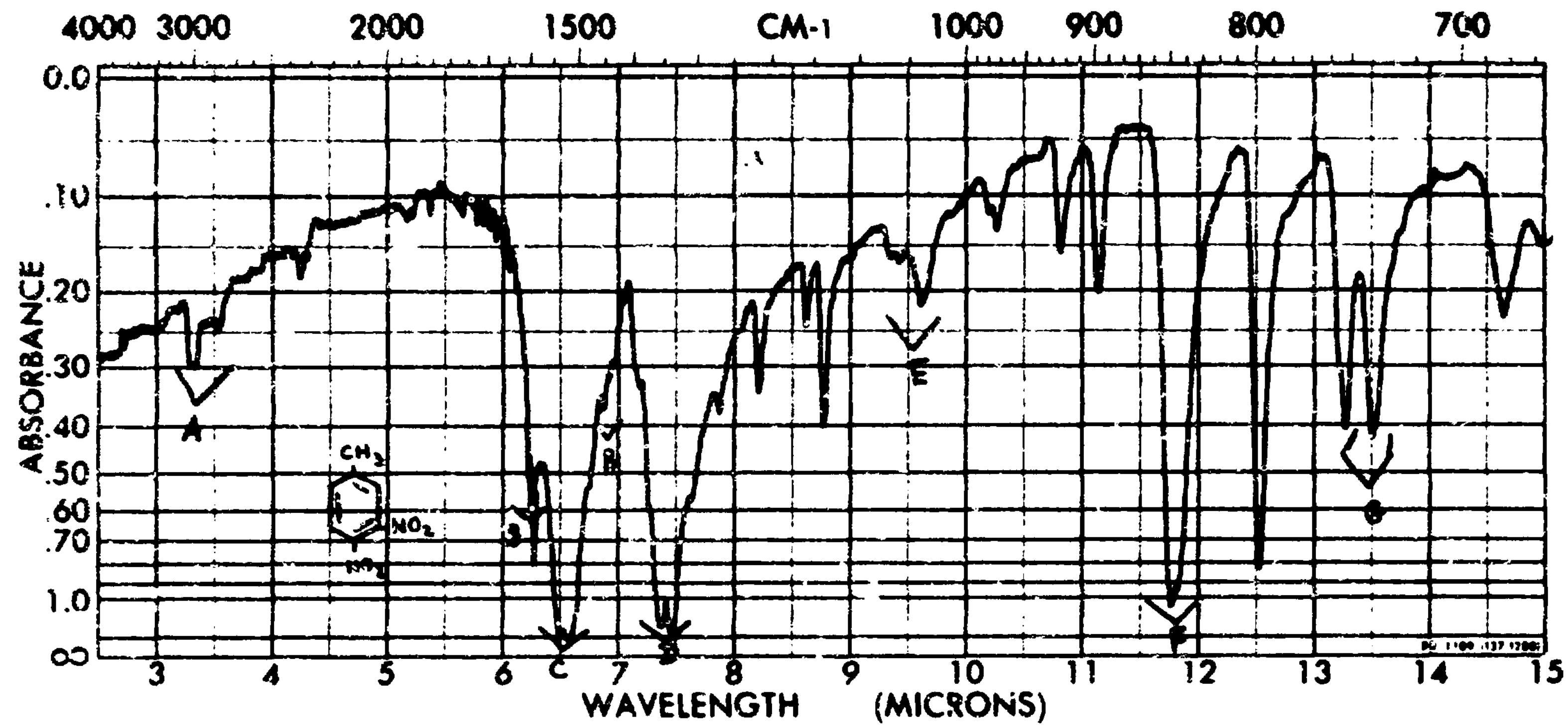
Anal. for $C_7H_6N_2O_4$: Calcd: C, 46.2; H, 3.3; N, 15.4
Found: C, 46.00; H, 3.35; N, 15.32.

High-Pressure Liquid Chromatography--One peak representing 100% of the total peak areas was observed by hplc. The following hplc conditions were used:

- Column: 4 mm × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Retention time: 517 sec 3,4-dinitrotoluene 100%.

Gas Chromatography--One major component (representing 99.8% of the total peak areas) and one minor component were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 837 sec 3,4-dinitrotoluene 99.8%; 757 sec impurity 0.2%.



SPECTRUM NO. 9	ORIGIN	LEGEND A: Aromatic & Methyl C-H stretch. 1. B: C=C ring stretch C: N=O stretch asymmetric. 2. D: N=O stretch symmetric	REMARKS E: In plane C-H bend, F: Ar NO2 C-N stretch, G: Out of plane C-H bend.
SAMPLE 3,4-DINITROTOLUENE (KBr PELLET)	PURITY		Less concentrated
I D K & K LABS, INC	PHASE	DATE MAY 10, 1977	
LOT 5739	THICKNESS	OPERATOR INGERSOLL	

SPECTRUM NO. 22
SAMPLE

RECORDING CHARTS

FIGURE 73 INFRARED SPECTRUM OF 3,4-DINITROTOLUENE

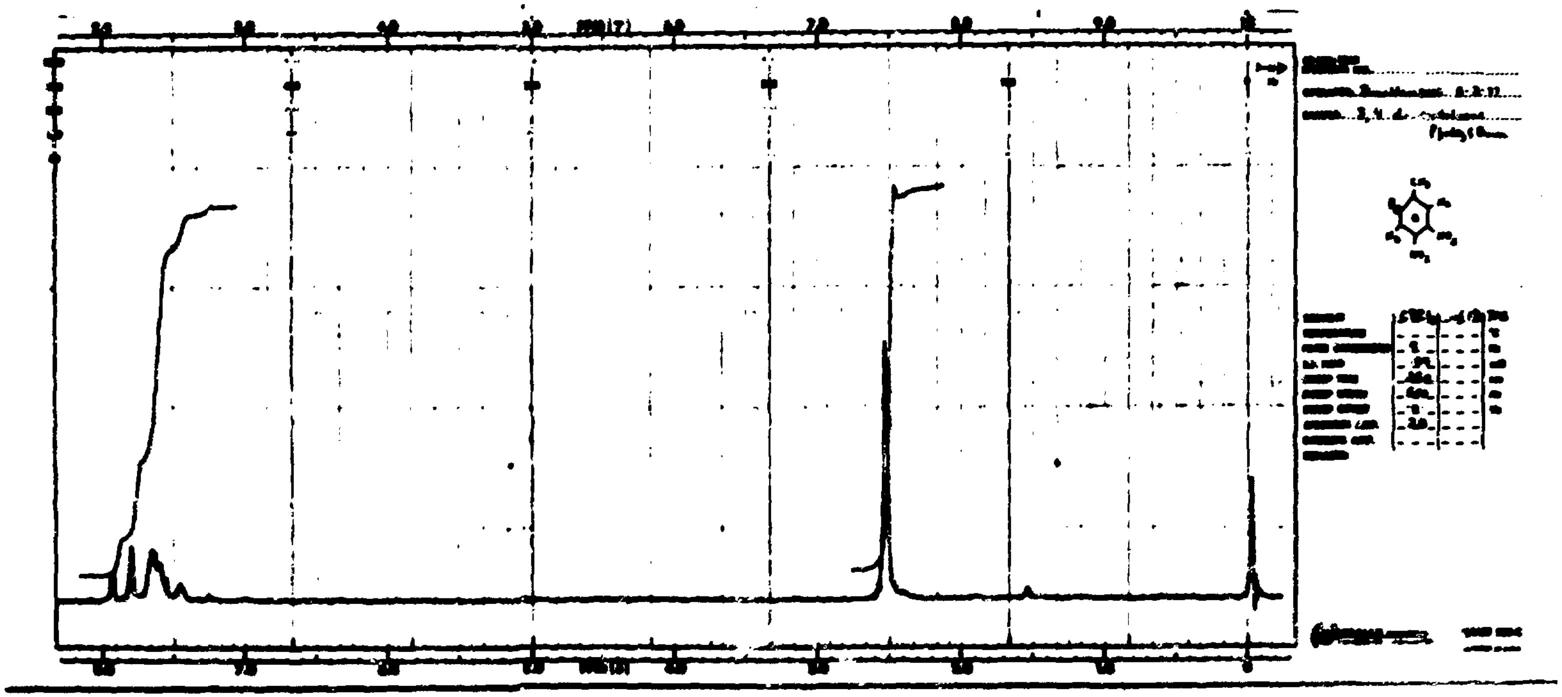


FIGURE 74 NMR SPECTRUM OF 3,4-DINITROTOLUENE

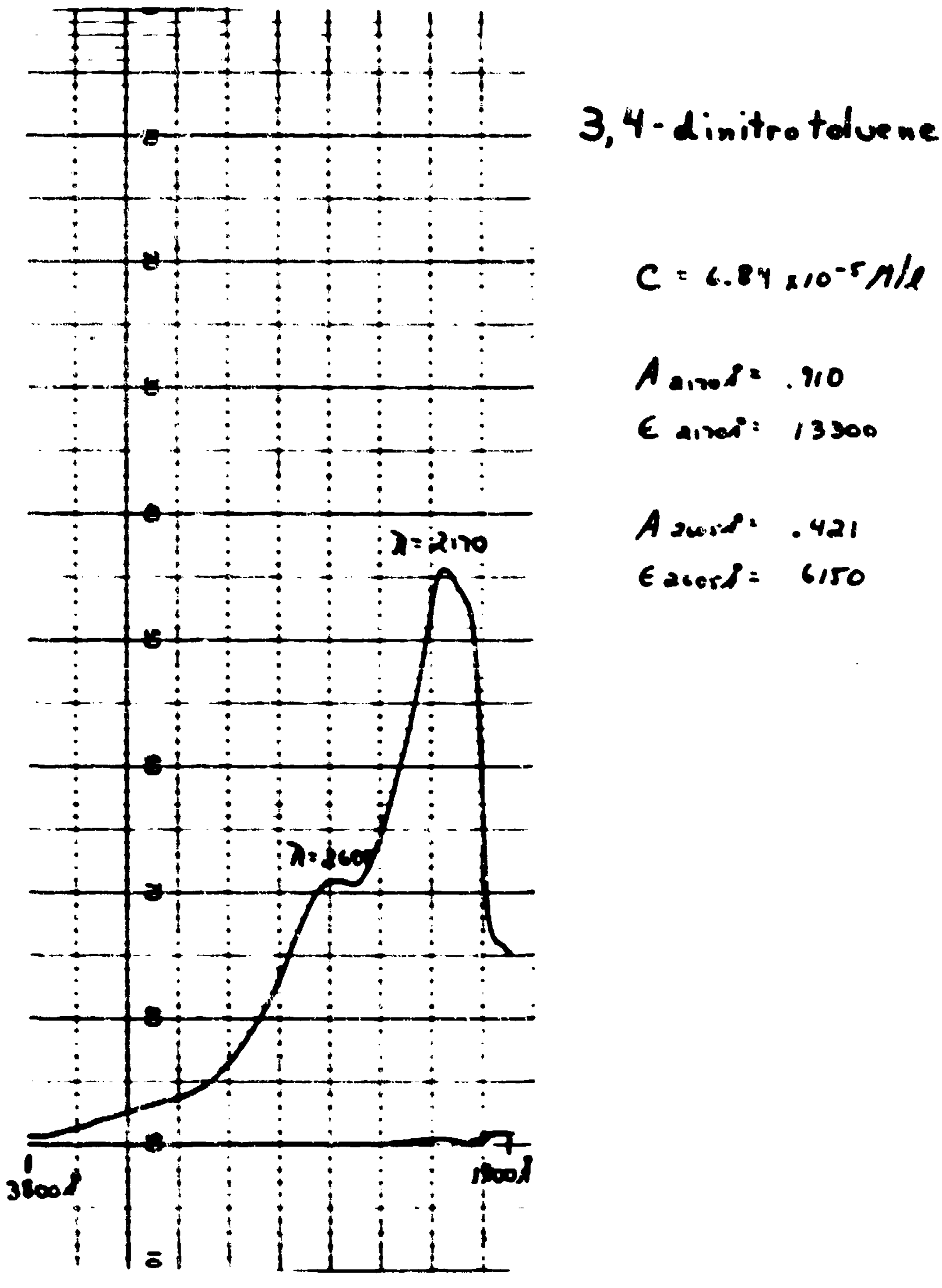


FIGURE 75 UV SPECTRUM OF 3,4-DINITROTOLUENE

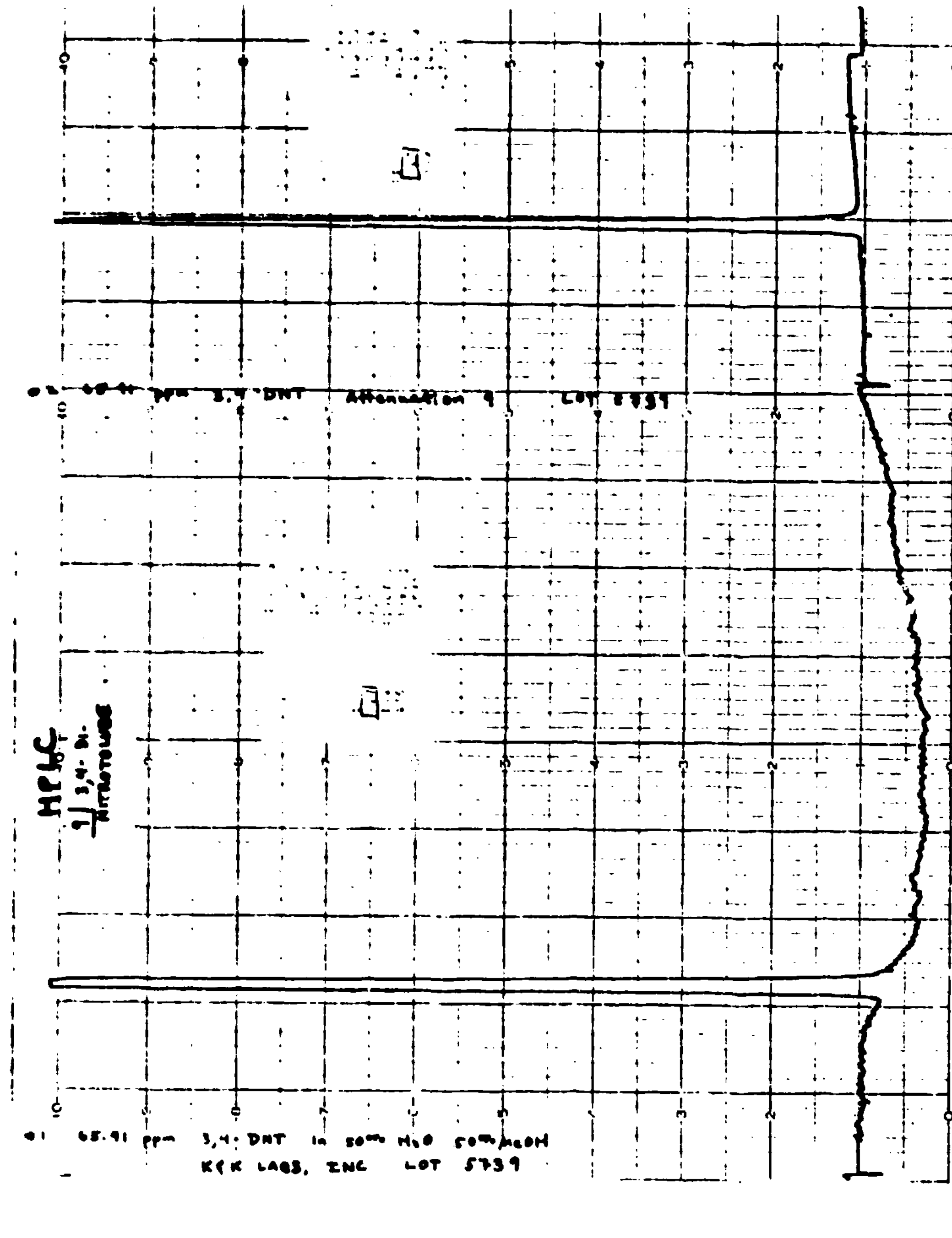
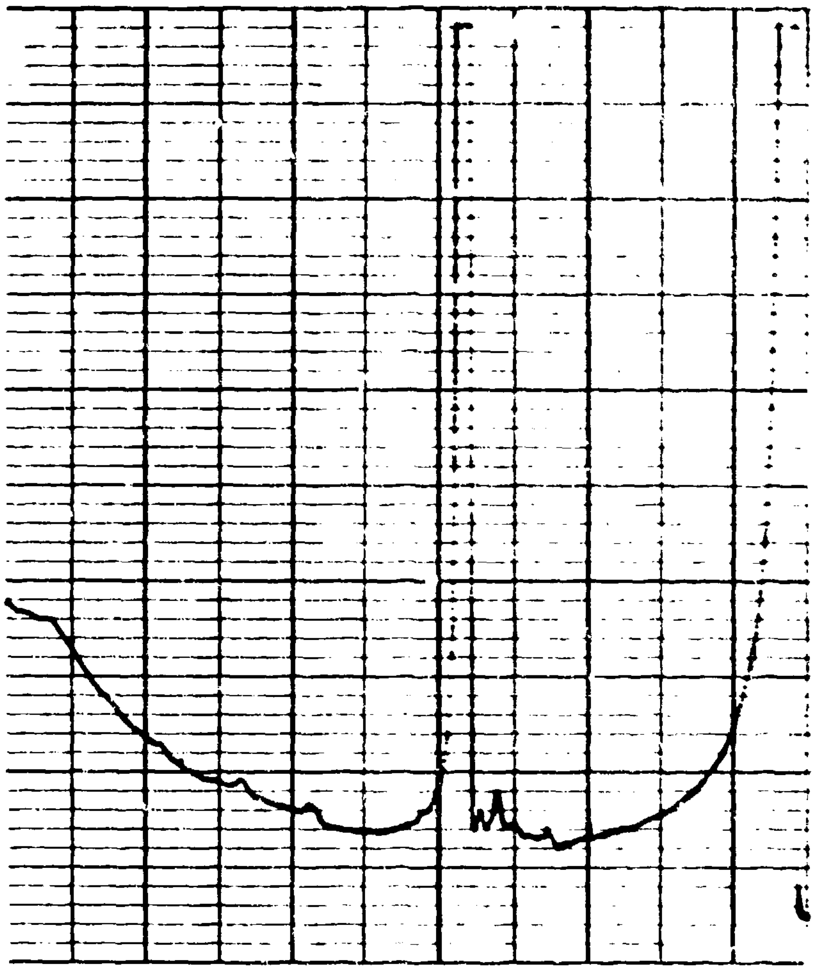


FIGURE 76 HPLC CHROMATOGRAM OF 3,4-DINITROTOLUENE

3,4 Dinitrotoluene



19	105775
26	4326006
27	1699084
757	509
837	256466
2411	729
	6586540

Operator: Donaldson 3-24-77
[redacted]
5
N_2 220 °C
20 220
10 3µl
Sample: 3,4-DNT 4

FIGURE 77 GC SPECTRUM OF 3,4-DINITROTOLUENE

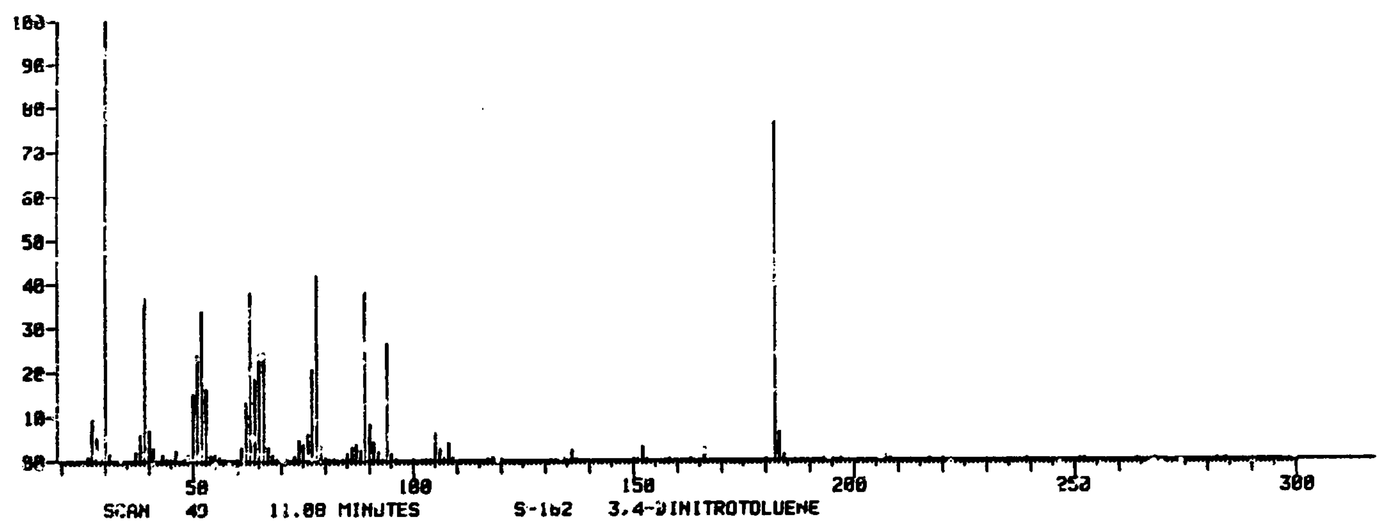
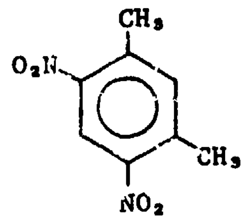
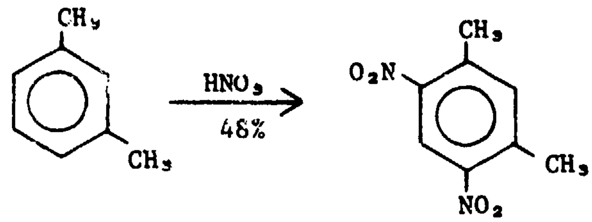


FIGURE 78 MASS SPECTRUM OF 3,4-DINITROTOLUENE

4.33 <u>4,6-Dinitro-m-Xylene</u>
1,5-Dimethyl-2,4-dinitrobenzene
[616-72-8]



Source: Synthesis, SRI



<u>Ir</u>--The ir spectrum was consistent with the proposed structure. The following bands were observed:

(1) (KBr pellet) 3.25 (=C-H, aromatic), 3.4, 3.5 (C-H, methyl), 6.2, 6.85 (C=C, ring), 6.5, 7.45 (N=O), 9.65, 13.4 (C-H), 11.62 (C-N, aromatic NO_2), 7.88, 8.55, 10.85, 11.3, 11.9, 12.9, 13.75, 14.35, 14.9 µm.

(2) (Thin film in $CHCl_3$) 5-6 (aromatic overtones) µm.

<u>Nmr</u>--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.72 (singlet, 6H) CH_3; δ 7.43 (singlet, H) H_a
δ 8.57 (singlet, H) H_b.

<u>uv (Methanol)</u>--λ_{max} = 207.4 nm, A = 0.926, ε = 8420
λ_{max} = 249.4 nm, A = 1.121, ε = 10,200.

<u>Purity</u> (99.0 ± 1%)

Elemental Analysis--

Anal. for $C_8H_8N_2O_4$: Calcd: C, 49.0; H, 4.1; N, 14.3

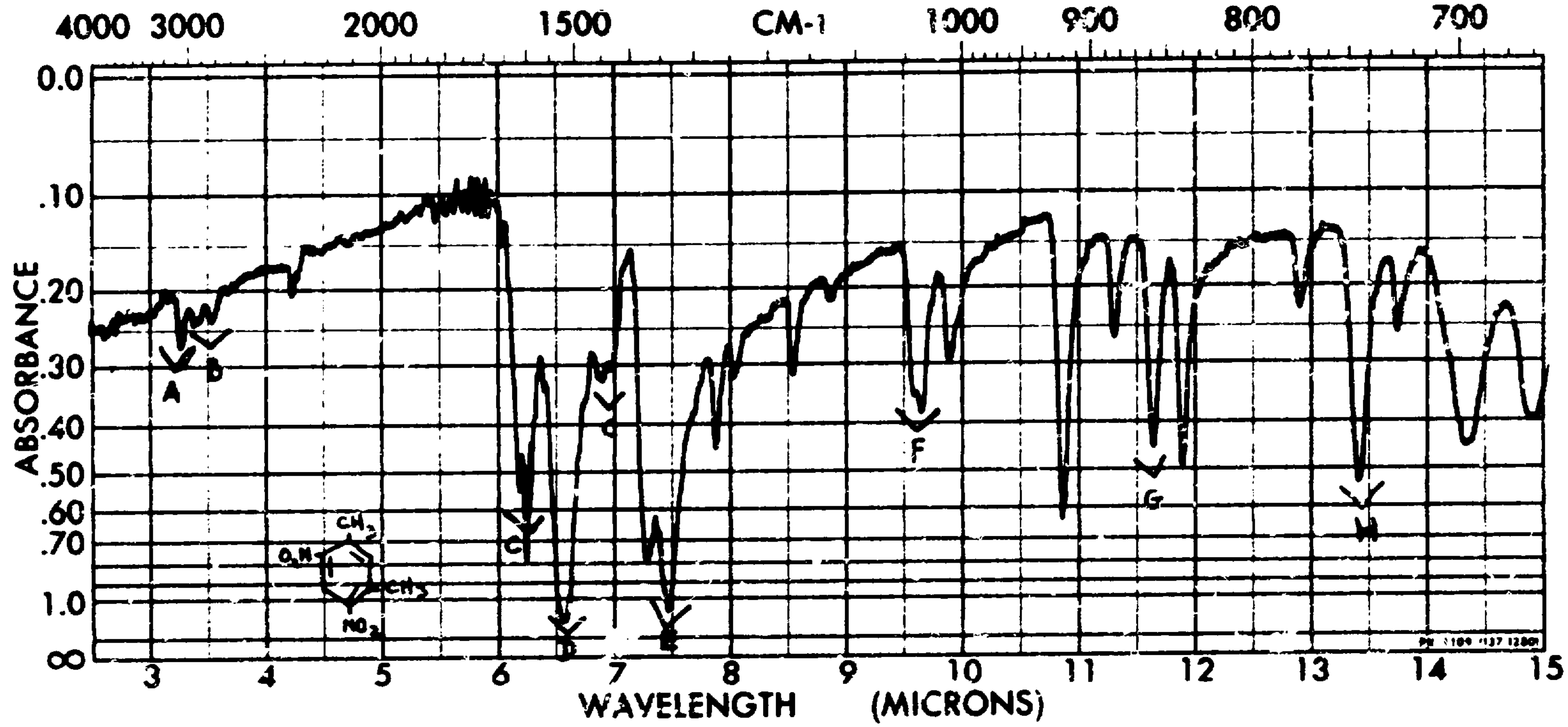
Found: C, 48.79; 4.13; N, 14.17.

High-Pressure Liquid Chromatography--One peak representing 100% of the total peak areas was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 853 sec 4,6-dinitro-m-xylene 100%.

Gas Chromatography--One major component (representing 98.0% of the total peak areas) and two minor components were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 110 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 1028 sec 4,6-dinitro-m-xylene 98.0%; 820 sec impurity 1.06%; 1442 sec impurity 0.94%.



SPECTRUM NO. 19	ORIGIN	LEGEND A: Aromatic C-H stretch	REMARKS slow SLIT = 1
SAMPLE 4,6-DINITRO-m-XYLENE (KBr PELLET)	PURITY	1. B: Methyl C-H stretch C: C=C RING stretch D: N=O stretch asymmetric 2. E: N=O stretch symmetric	F: In plane C-H bend
I.D.: LOT SRI #2	PHASE	DATE MAY 11, 1977	G: Ar-NO2 C-N stretch
	THICKNESS	OPERATOR INGERSOLL	H: Out of plane C-H bend.

SPECTRUM NO. 44
SAMPLE

FIGURE 79 INFRARED SPECTRUM OF 4,6-DINITRO-m-XYLENE

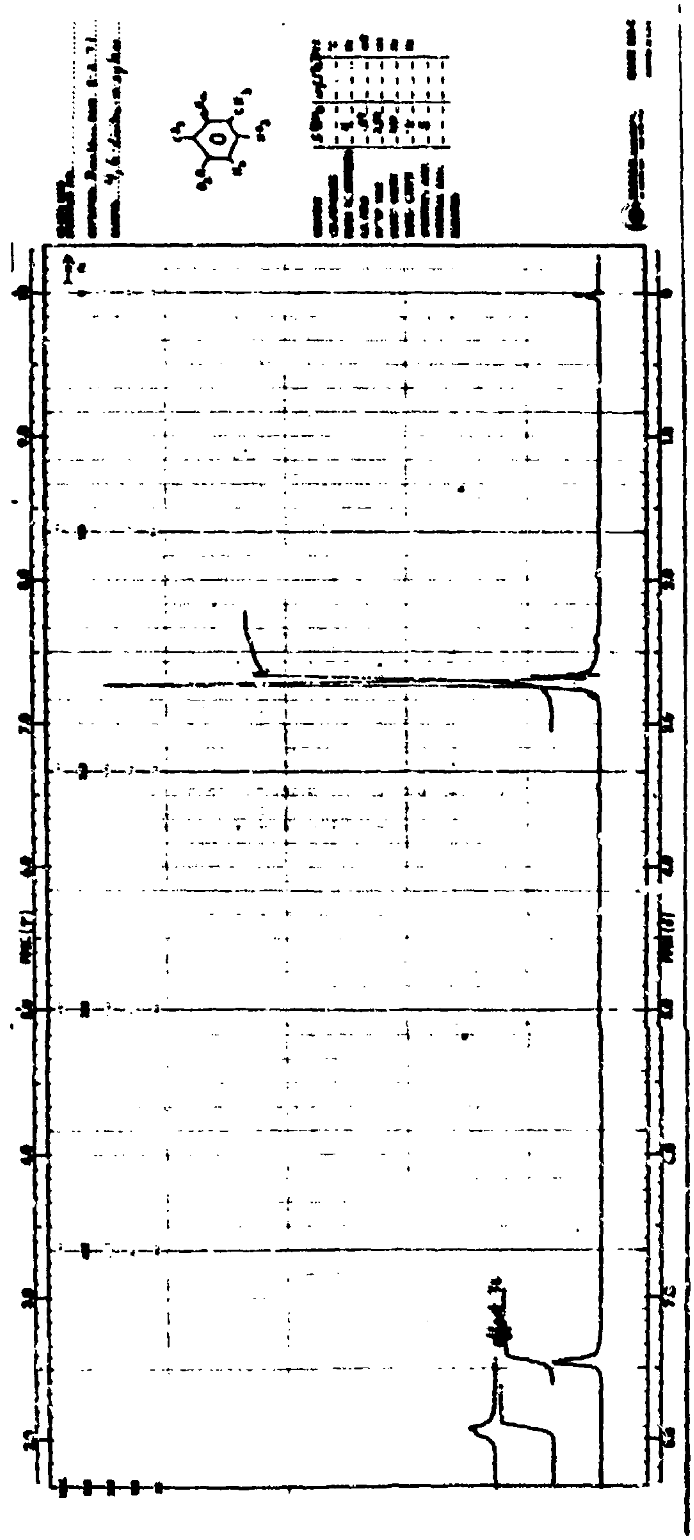


FIGURE 80 NMR SPECTRUM OF 4,6-DINITRO-m-XYLENE

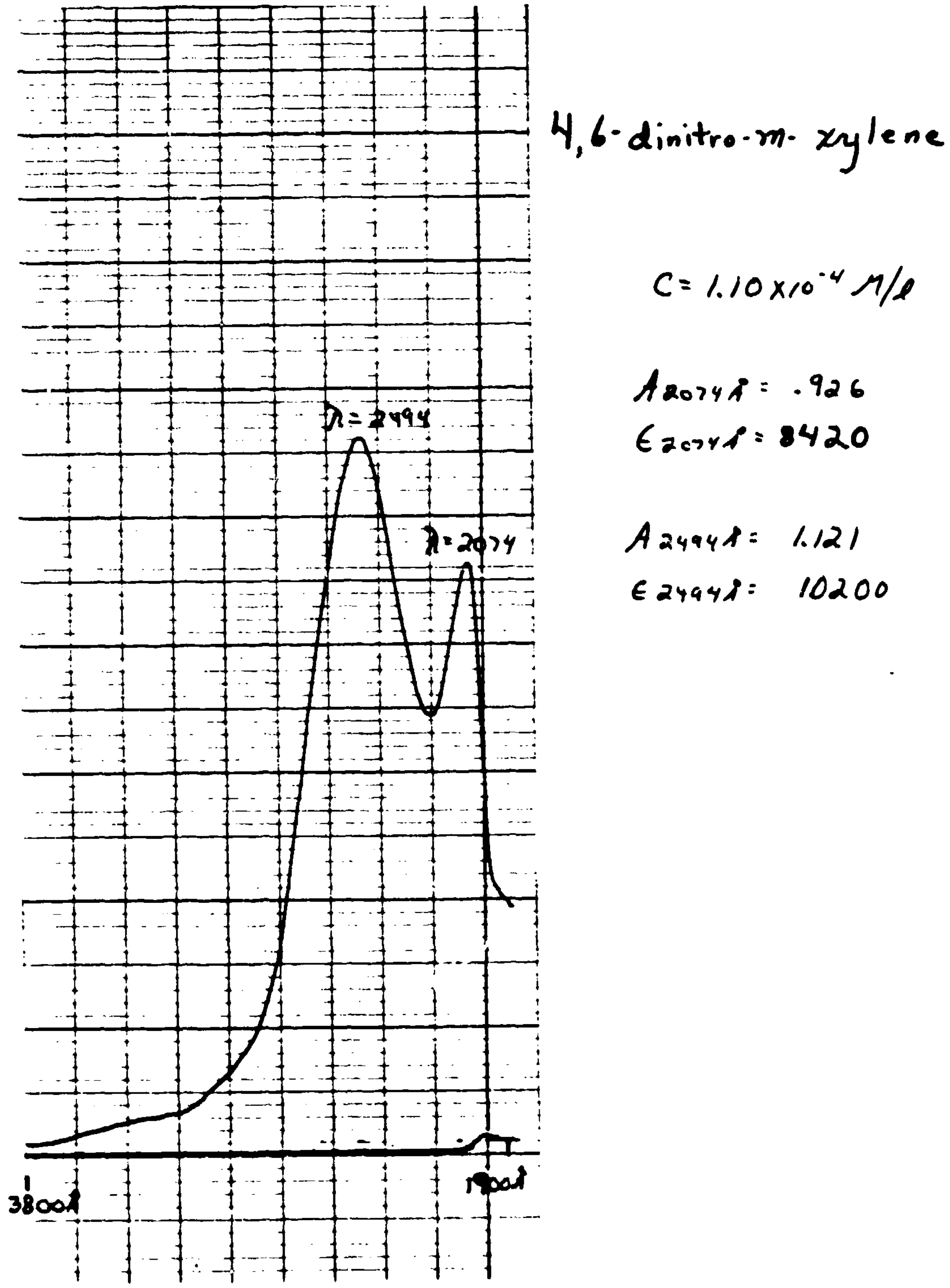


FIGURE 81 UV SPECTRUM OF 4,6-DINITRO-m-XYLENE

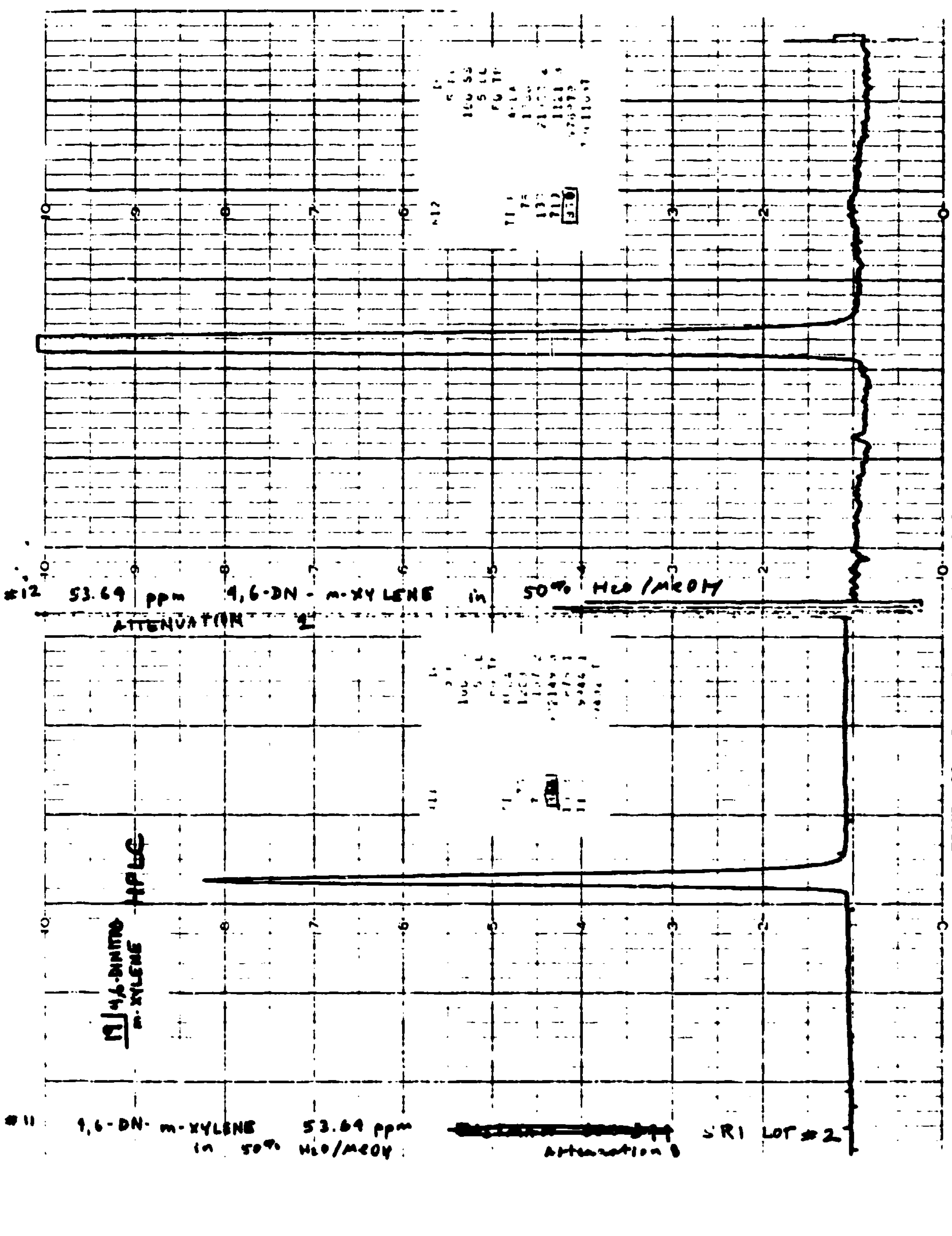


FIGURE 82 HPLC CHROMATOGRAM OF 4,6-DINITRO-m-XYLENE

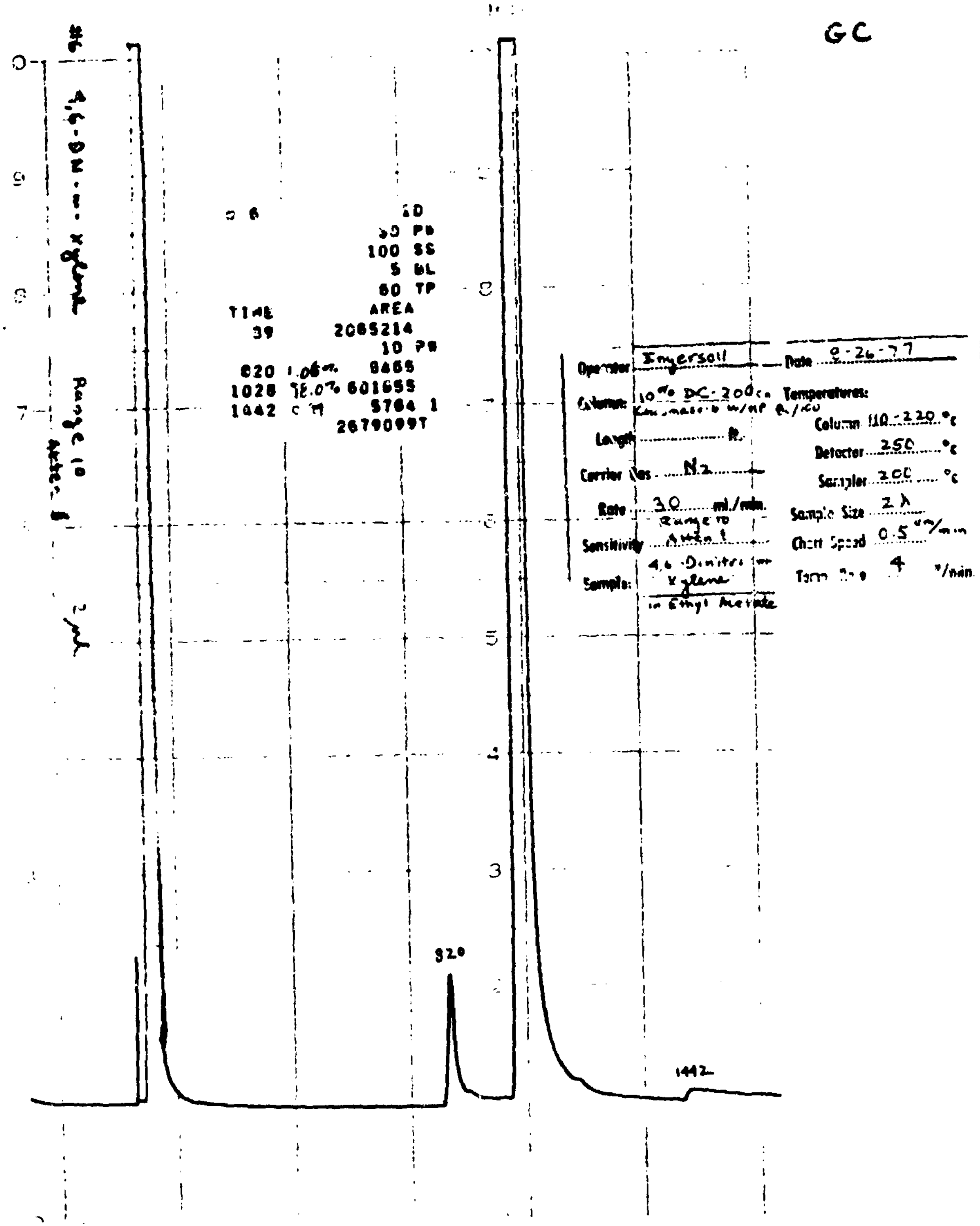


FIGURE 83 GC SPECTRUM OF 4,6-DINITRO-m-XYLENE

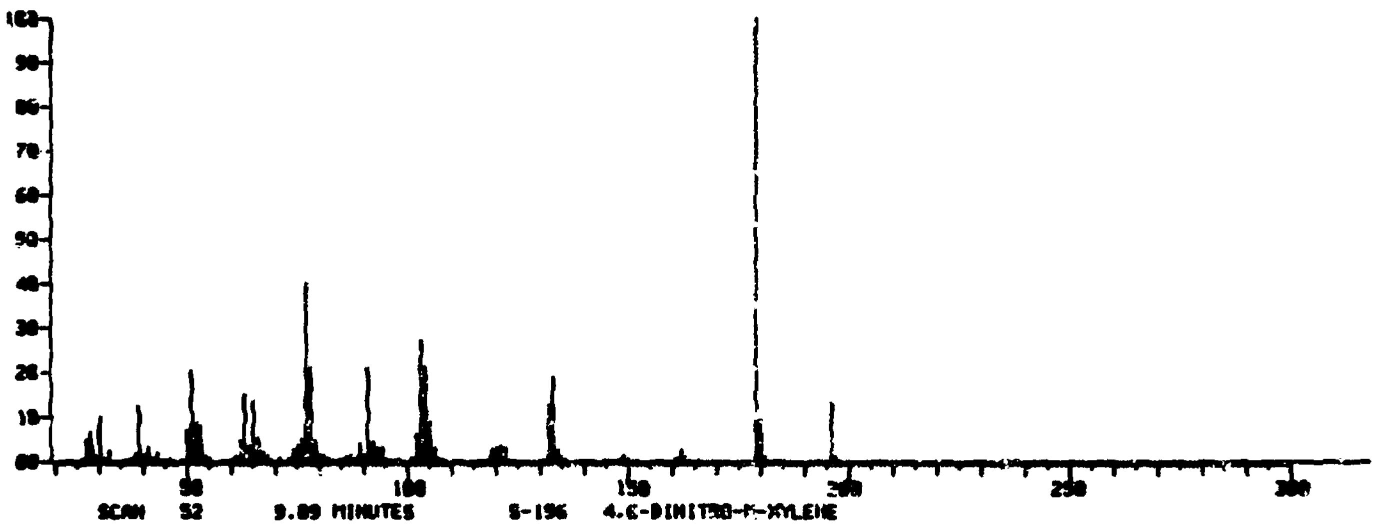
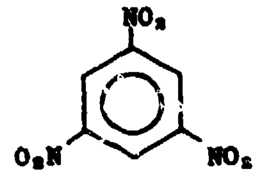
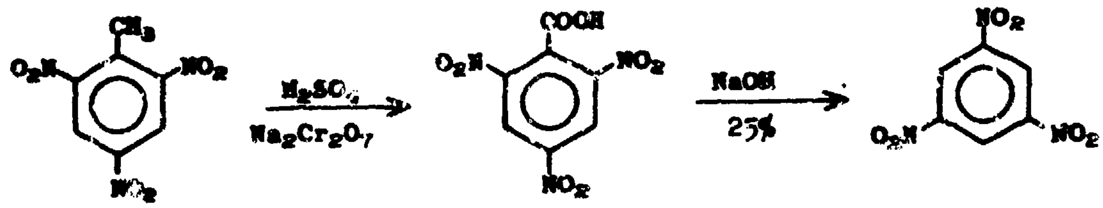


FIGURE 84 MASS SPECTRUM OF 4,6-DINITRO-m-XYLENE

4.14 1,3,5-Trinitrobenzene
[99-35-4]



Source: Synthesis, SRI



Identity

Ir--The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference No. 1086 for 1,3,5-trinitrobenzene (mulled in mineral oil). The following bands were observed:

(1) (KBr pellet) 3.3 (=C-H, aromatic), 6.2, 6.95 (C=C, ring), 6.5, 7.5 (N=O), 9.35 (C-H), 5.0, 10.9, 13.2, 13.7, 14.0 μm.

(2) (KBr pellet) 5-6 (aromatic overtones, possibly 1,3,5-benzenoid substitution) μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 9.36 (singlet, 3H) H.

uv (Methanol)--λ_{max} = 222.8 nm, A = 1.775, ε = 27,200.

Purity (100%)

Elemental Analysis--

Anal. for $C_6H_3N_3O_6$: Calcd: C, 33.81; H, 1.42; N, 19.72

Found: C, 33.95; H, 1.44; N, 17.93.

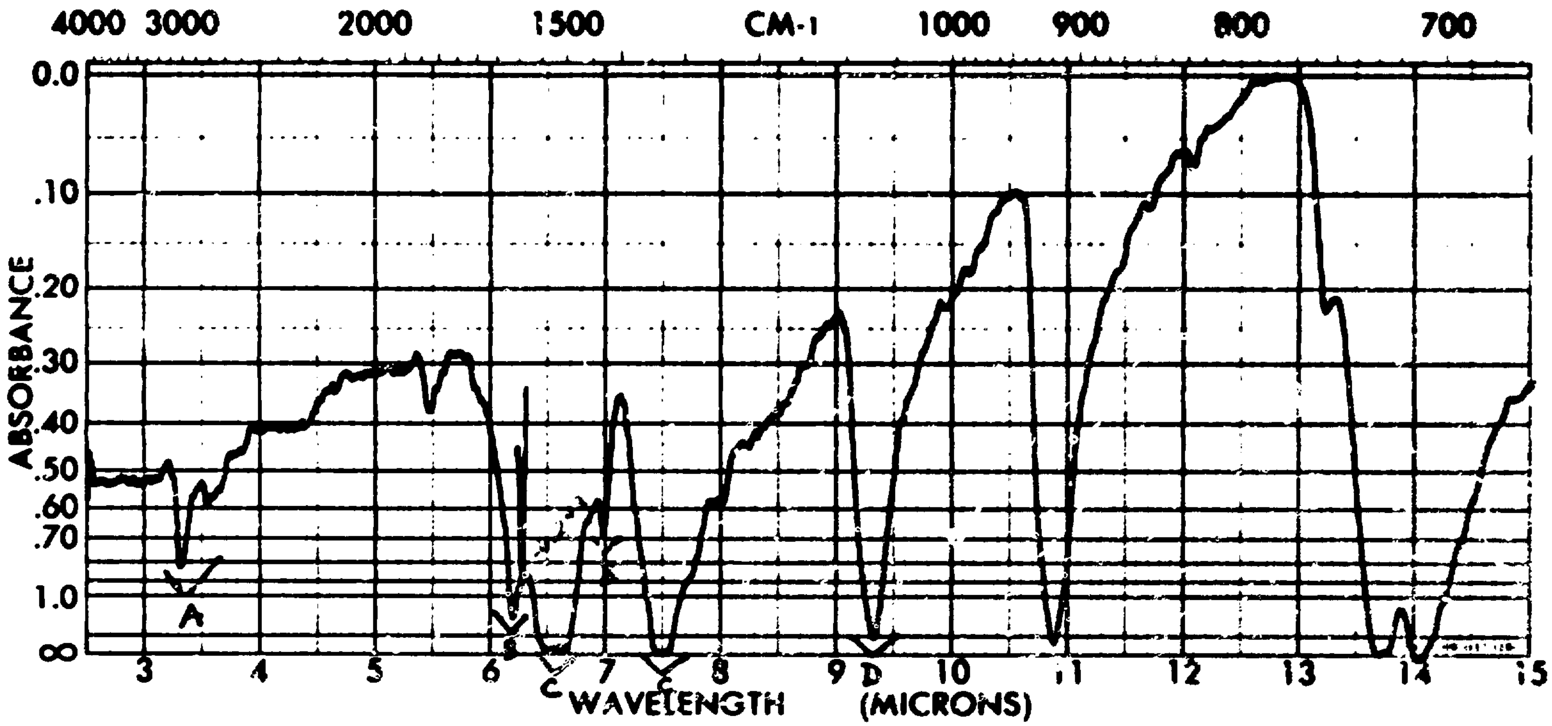
Trinitro compounds give low N analysis on the Perkin Elmer CHN analyzer.

High-Pressure Liquid Chromatography--One peak (representing 100% of the total peak areas) was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.2 ml/min
- Detection: uv at 254 nm
- Retention time: 326 sec 1,3,5-trinitrobenzene 100%.

Gas Chromatography--One peak (representing 100% of the total peak areas) was observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 939 sec 1,3,5-trinitrobenzene 100%.



SPECTRUM NO.	ORIGIN	LEGEND A: Aromatic C-H stretch	REMARKS
SAMPLE 1,3,5-TRINITROBENZENE KBr PELLET		1. B: C=C ring stretch C: N=O stretch	
	PURITY	2. D C-H bend (in plane)	
	PHASE	DATE AUGUST 29, 1977	
	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO.
SAMPLE

FIGURE 85 INFRARED SPECTRUM OF 1,3,5-TRINITROBENZENE

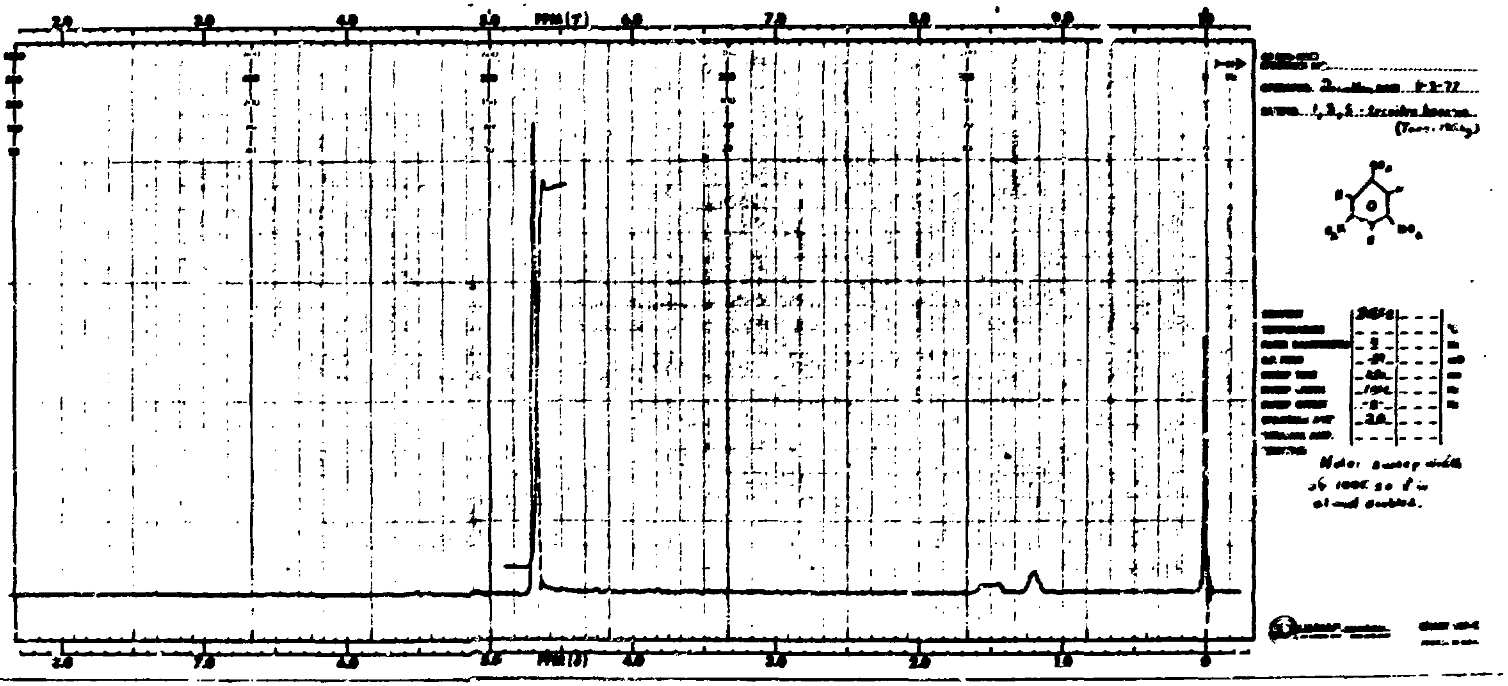


FIGURE 86 NMR SPECTRUM OF 1,3,5-TRINITROBENZENE

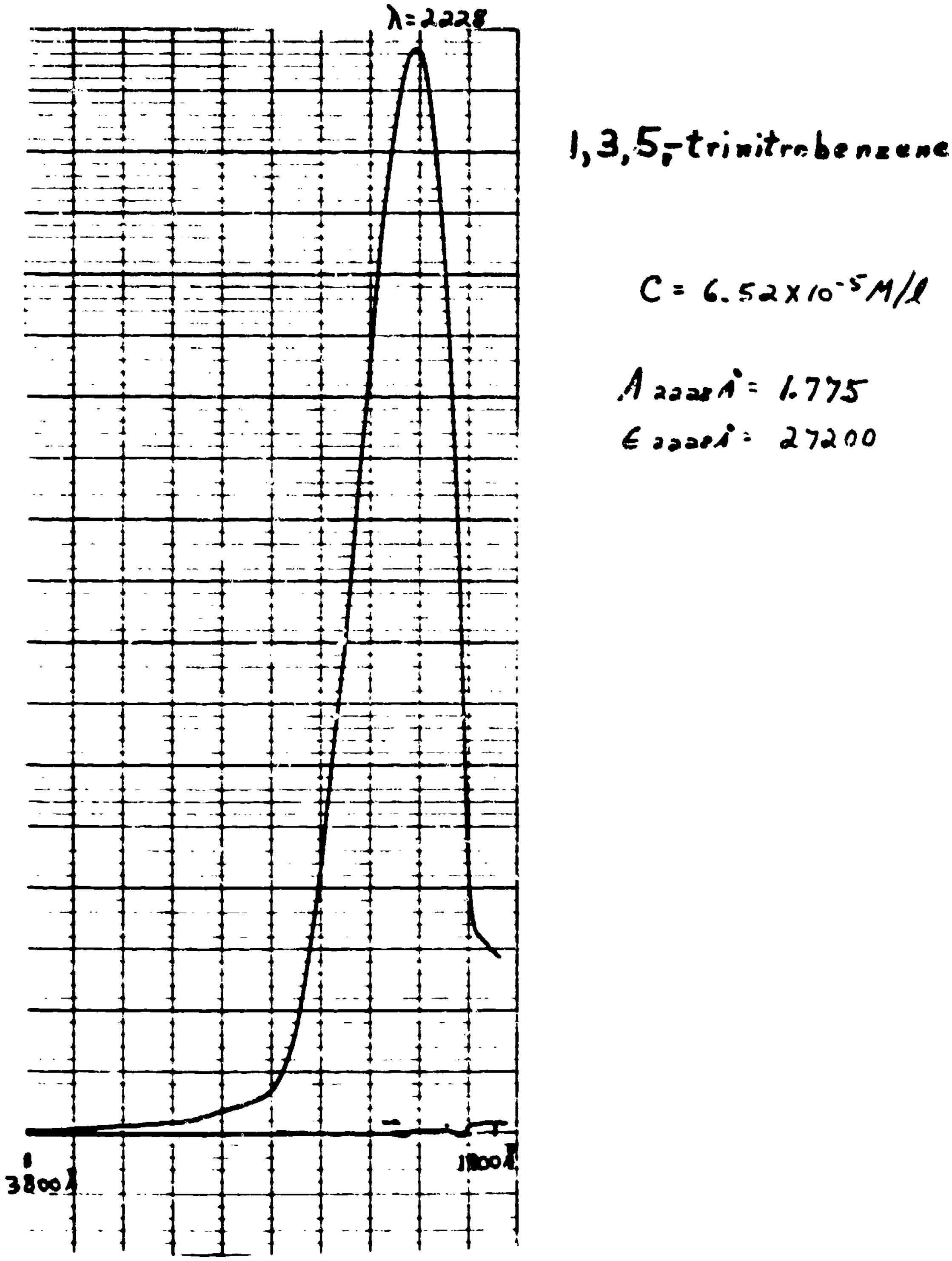


FIGURE 87 UV SPECTRUM OF 1,3,5-TRINITROBENZENE

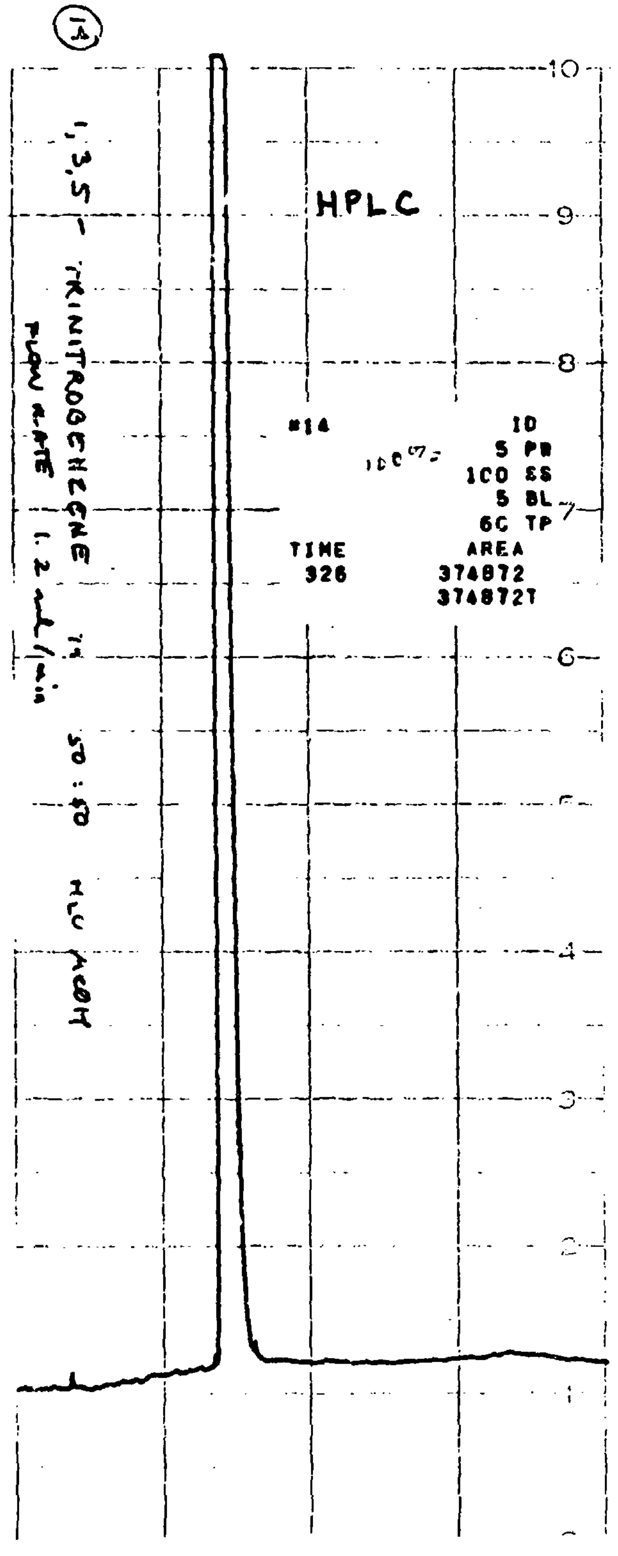
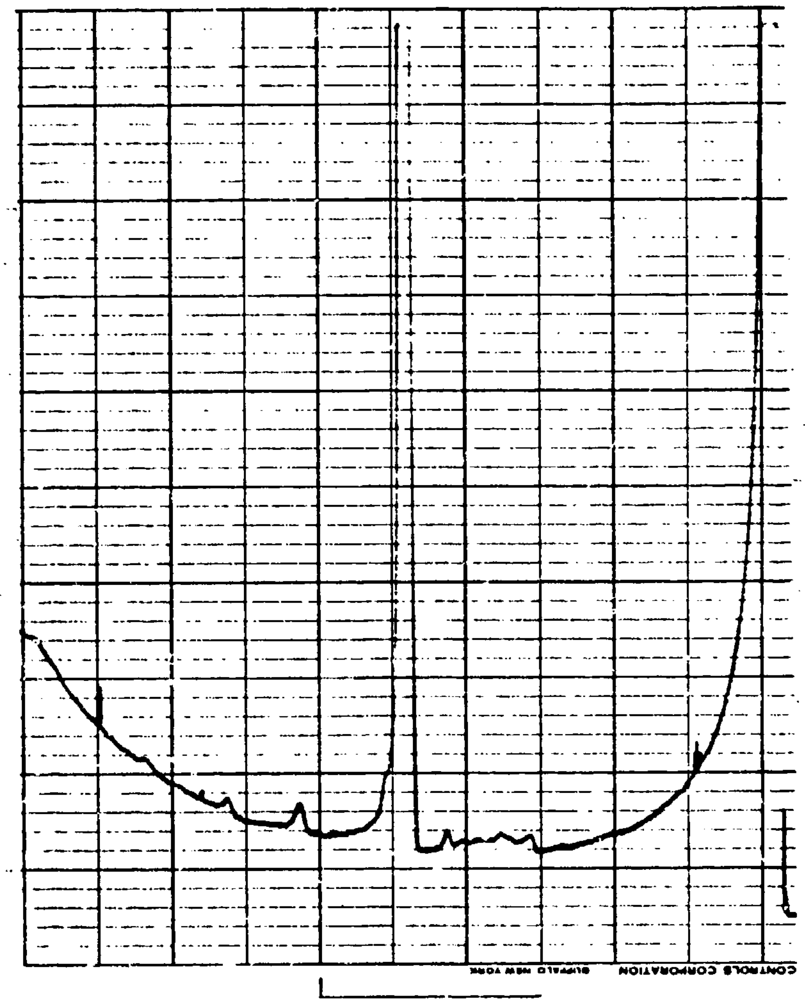


FIGURE 88 HPLC CHROMATOGRAM OF 1,3,5-TRINITROBENZENE

19

GC
1, 3,5 Trinitrobenzene



27	5334590
236	163
939	259223
1204	621

Operator Donaldson Date 3-28-77

Column: [redacted] DC-200 HB/... Temperatures:

Length 5 ft. Column 120-220°c

Carrier Gas N_2 Detector 220 °c

Rate 20 ml./min. Sampler 200 °c

Sample Size 2µl

Sensitivity 10^{-10}, ... Chart Speed .16 in/min

Sample 1,3,5-TNB Temp. Rate 4 °/min

FIGURE 89 GC SPECTRUM OF 1,3,5-TRINITROBENZENE

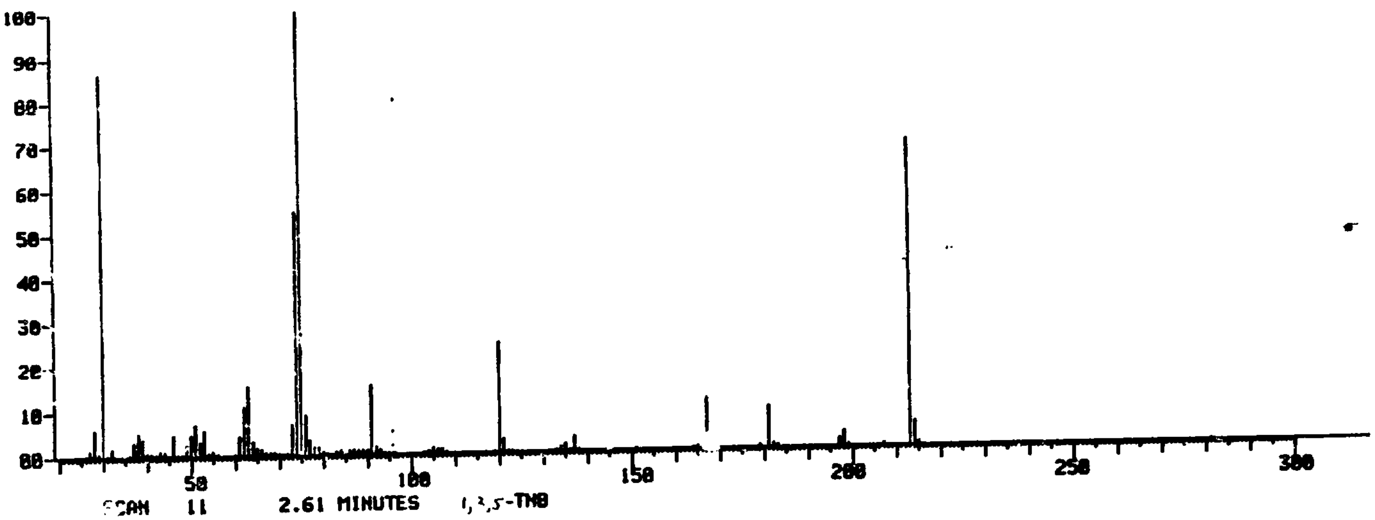
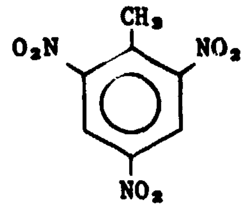


FIGURE 90 MASS SPECTRUM OF 1,3,5-TRINITROBENZENE

4.15 2,4,6-Trinitrotoluene
2-Methyl-1,3,5-trinitrobenzene
[118-96-7]



Source: E. I. duPont
Lot number not available

Identity (recrystallized)

Ir--The ir spectrum was consistent with the proposed structure as well as with Sadtler Reference No. 21886 for 2,4,6-dinitrotoluene (between salts). The following bands were observed: (KBr pellet) 3.3 (=C-H, aromatic), 6.2, 6.85 (C=C, ring) 6.5, 7.4 (N=O), 13.6 (C-H), 8.3, 8.55, 10.6, 10.99, 12.58, 13.9 μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.39 (singlet, CH_3); δ 8.78 (singlet, H_a).

uv (Methanol)--λ_{max} = 226.0 nm, A = 1.793, ε = 18,700.

Purity--(Recrystallized, 99.995 ± 0.05%; crude, 99.6%)

Elemental Analysis--

Anal. for $C_7H_5N_3O_6$: Calcd: C, 37.01; H, 2.22; N, 18.50
Found: C, 36.95; H, 2.26; N, 17.93.

Trinitro compounds give low N results with the Perkin-Elmer CHN analyzer.

High-Pressure Liquid Chromatography--(2,4,6-Trinitroluene, recrystallized.) One major component (representing 99.9% of the total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

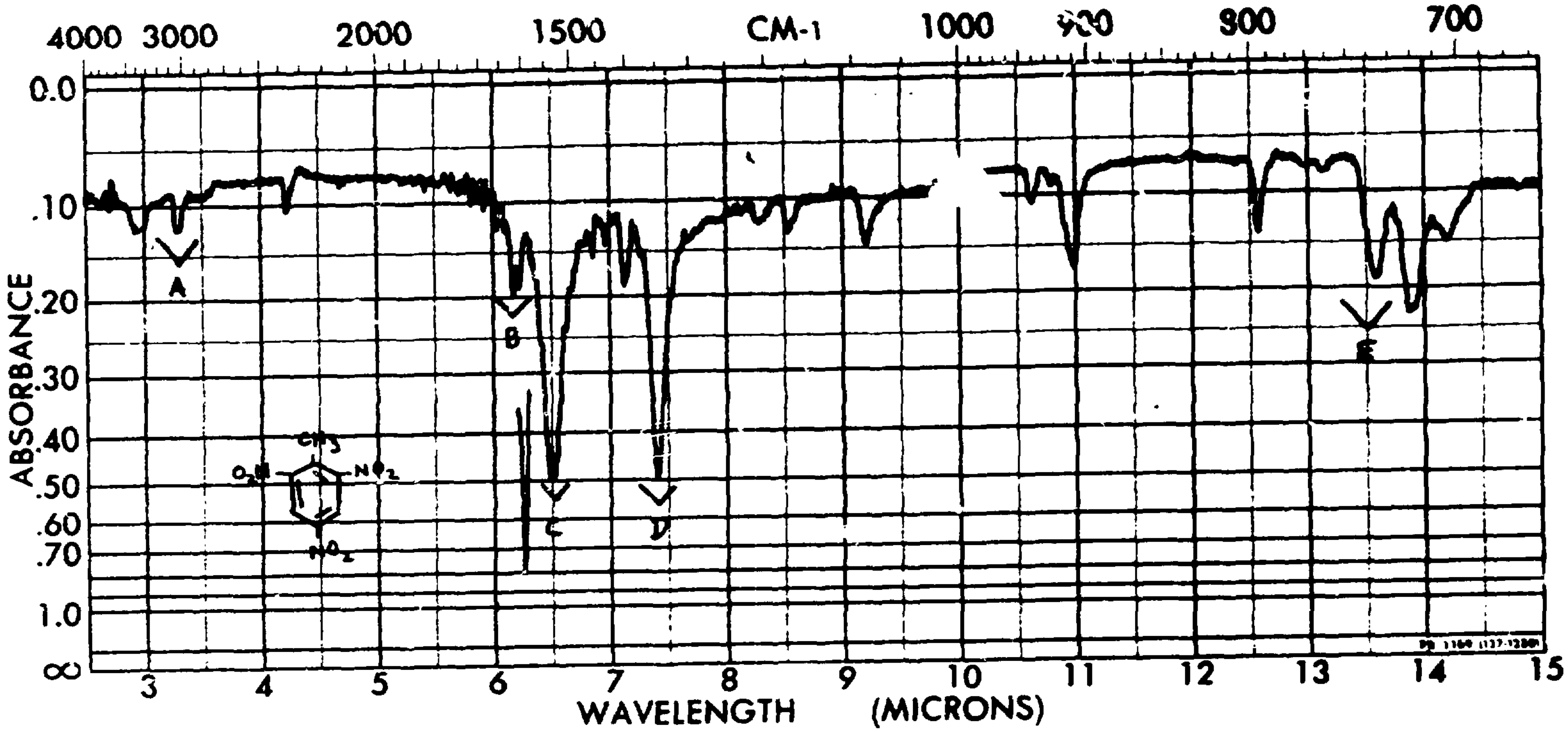
- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 442 sec 2,4,6-dinitrotoluene 99.9%; 69 sec impurity 0.1%.

Gas Chromatography--

Crude 2,4,6-trinitrotoluene--One major component (representing 99.6% of the total peak areas) and one minor component were observed by gc.

Recrystallized 2,4,6-trinitrotoluene--One major peak (representing 100% of the total peak areas) was observed by gc. The following gc conditions were used in both cases:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 100 to 220°C at 4°/min.
- Flow rate: 20 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 988 sec crude 2,4,6-trinitrotoluene 99.6%; 763 sec impurity 0.4%; 1024 sec recrystallized 2,4,6-trinitrotoluene 100%.



SPECTRUM NO. 10	ORIGIN	LEGEND	REMARKS slow slit = 1
SAMPLE α- TNT recrystallized	2,4,6-TRINITROTOLUENE	1.	A: Aromatic C-H stretch
(KBr PELLET)	PURITY	2.	B: C=C ring stretch
	PHASE	DATE MAY 11, 1977	C: NO stretch asymmetric
	THICKNESS	OPERATOR INGERSOLL	D: N=O stretch symmetric
			E: Out of plane C-H bend

SPECTRUM NO. 23
SAMPLE

FIGURE 91 INFRARED SPECTRUM OF 2,4,6-TRINITROTOLUENE

RECORDING CHARTS

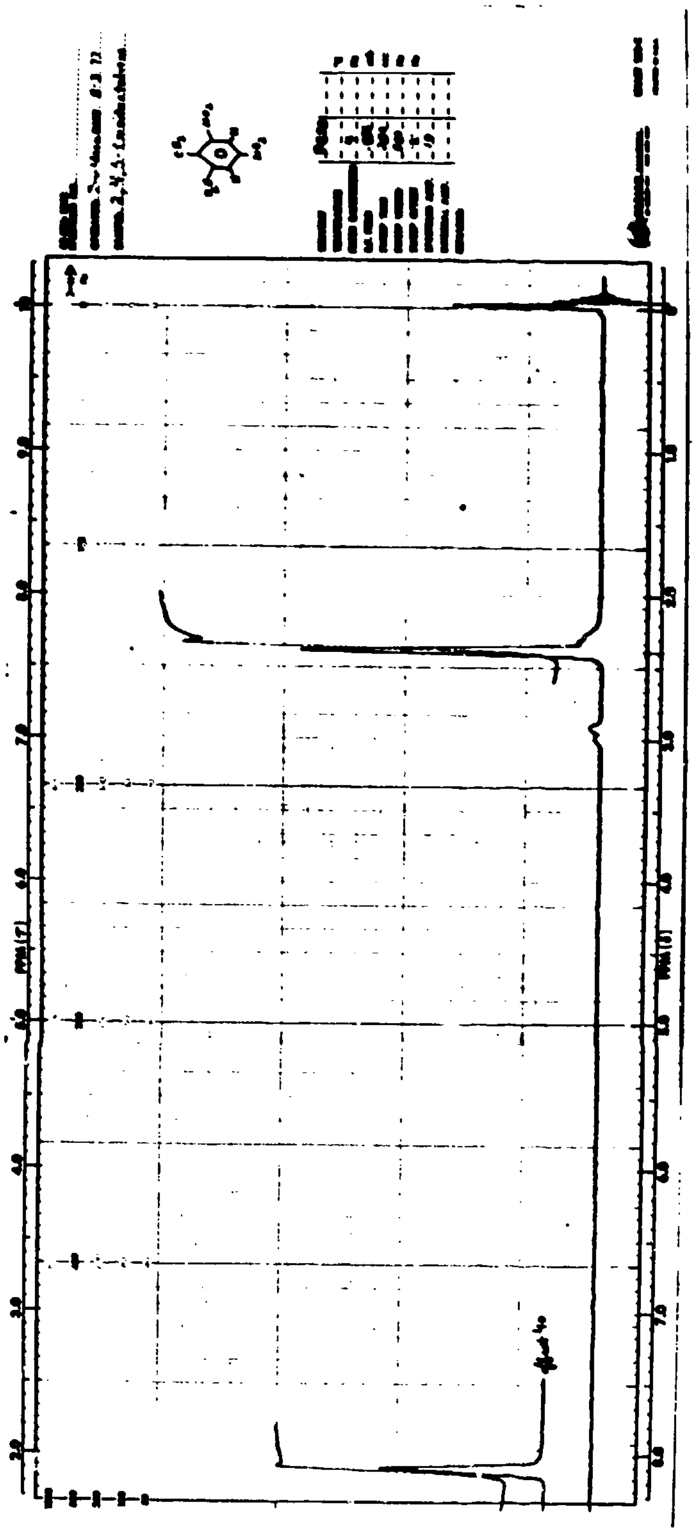


FIGURE 92 NMR SPECTRUM OF 2,4,6-TRINITROTOLUENE

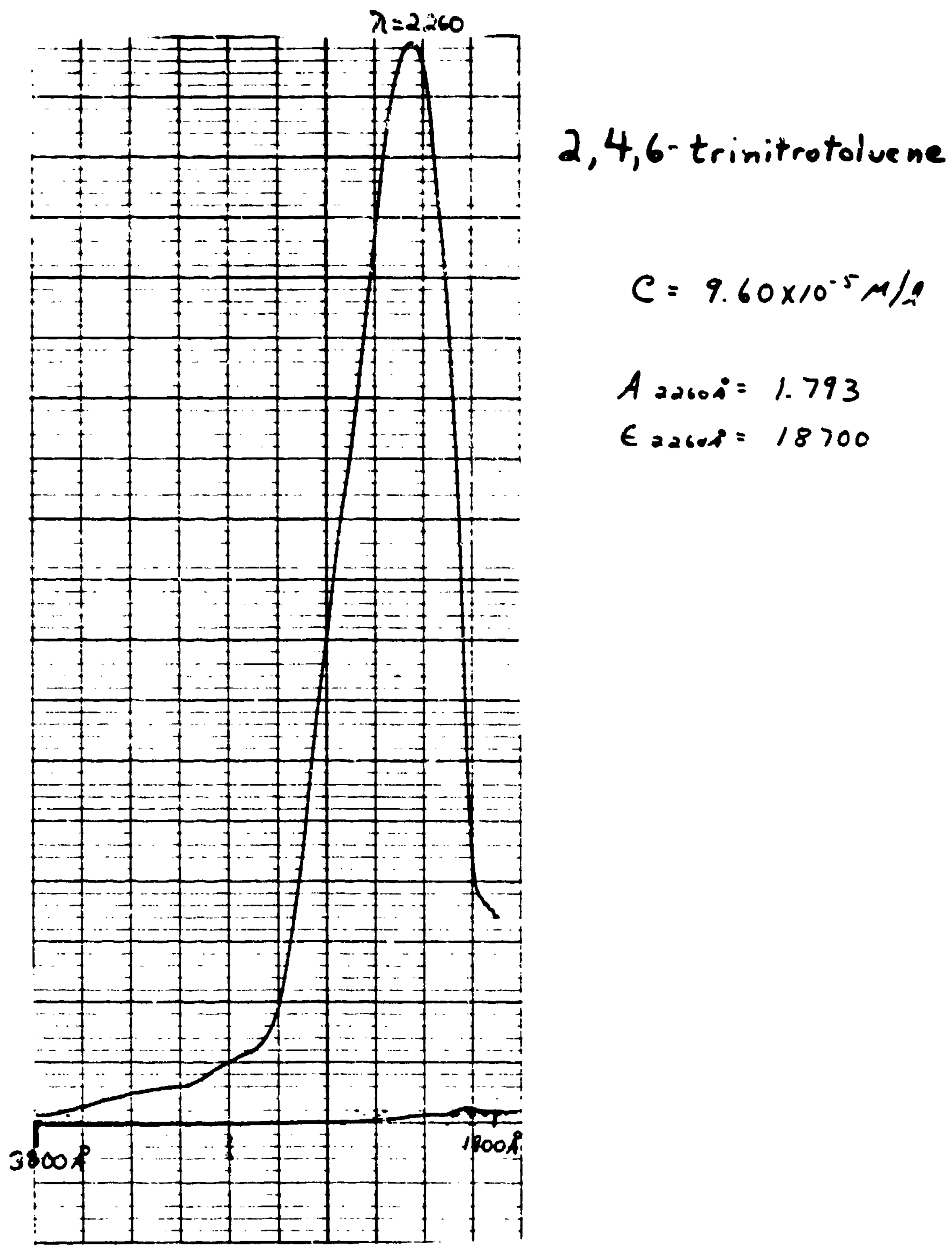
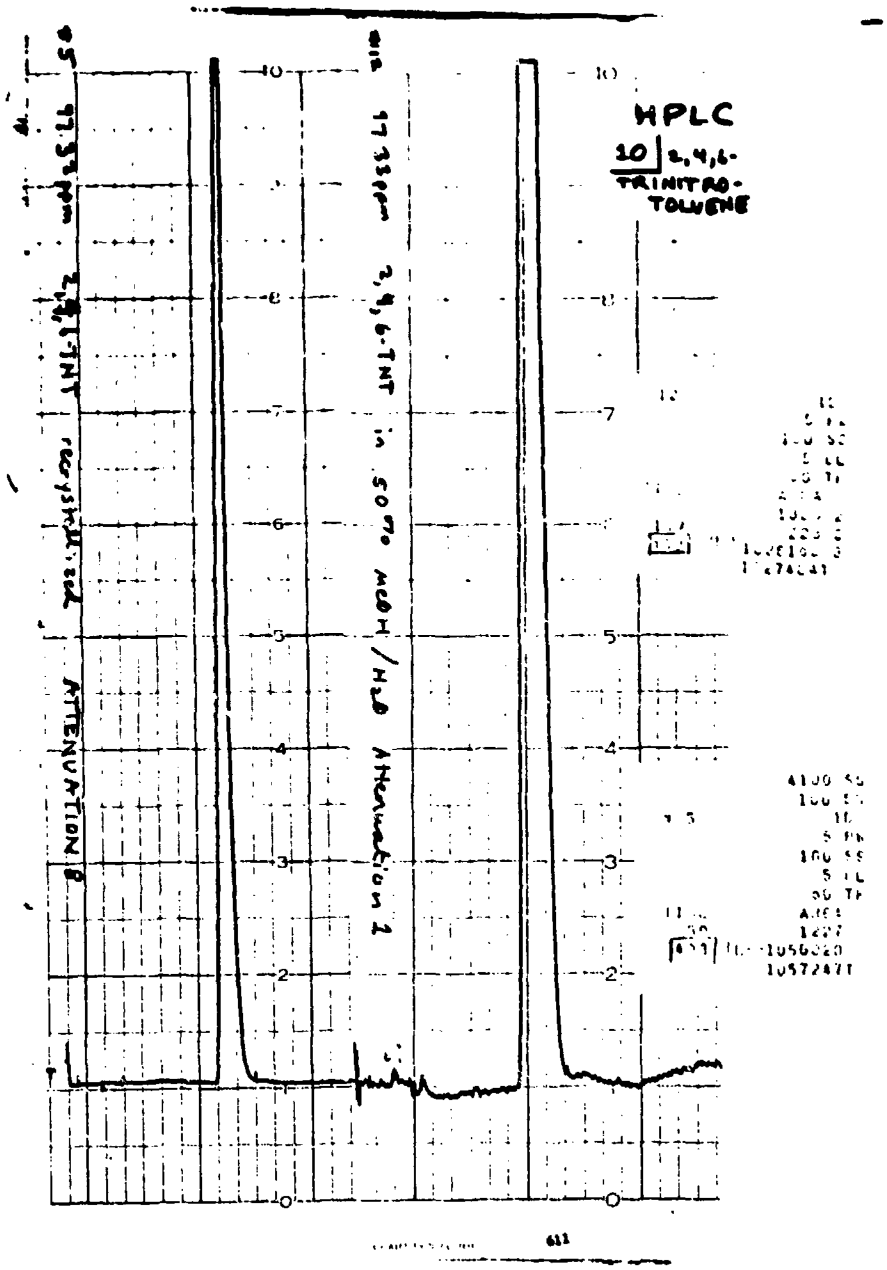


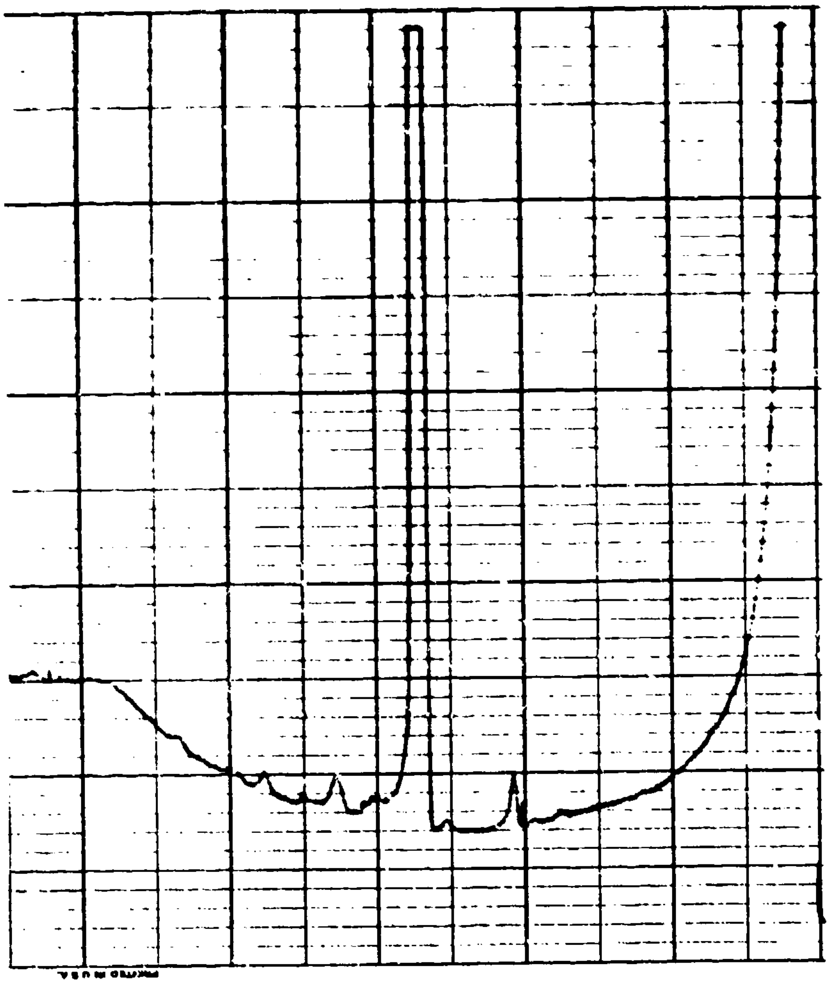
FIGURE 93 UV SPECTRUM OF 2,4,6-TRINITPOTOLUENE



...URE 94 HPLC CHROMATOGRAM OF 2,4,6-TRINITROTOLUENE

GC

Crude 2,4,6 Trinitrotoluene



18	111
26	6662294
763	1119
985	256945
1196	649
2020	
	6951310

Operator Donaldson Date 3-28-77

Column: [redacted]
10% DC-200 HP 80/100

Temperatures:

Length 5 ft.

Column 100-220°c

Detector 220 °c

Carrier Gas N_2

Sampler 200 °c

Rate 20 ml/min.

Sample Size 3 µl

Sensitivity 10^{-10}, Atten 1

Chart Speed .16 in/min

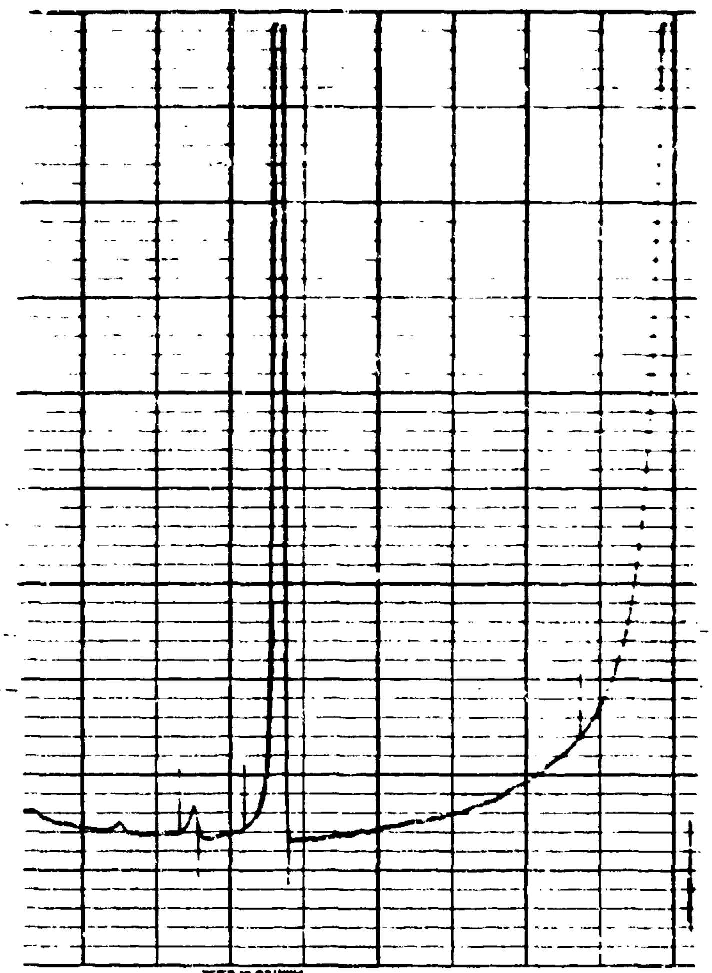
Sample: crude 2,4,6 TNT

Temp. Rate °/min.

FIGURE 95 GC SPECTRUM OF CRUDE 2,4,6-TRINITROTOLUENE

GC

Recrystallized 2,4,6 Trinitrotoluene



21	
31	8528793
1024	63625
1232	645
1664	1
5636	131
	65995 0

Operator: Donaldson   Date: 3-28-77

Column: [redacted] 10% DC 200   Temperatures:

Length: 5 ft.   Col: 100-220 °c

Detector: 220 °c

Carrier Gas: N_2 Injector: 200 °c

Rate: 20 ml/min.   Sample size: 2 µl

Sensitivity: 10^{-10}, Attn 1   Chart speed: .16 in/min

Sample: pure 2,4,6 TNT   Temp. rate: 4 °/m

FIGURE 96 GC SPECTRUM OF RECRYSTALLIZED 2,4,6-TRINITROTOLUENE

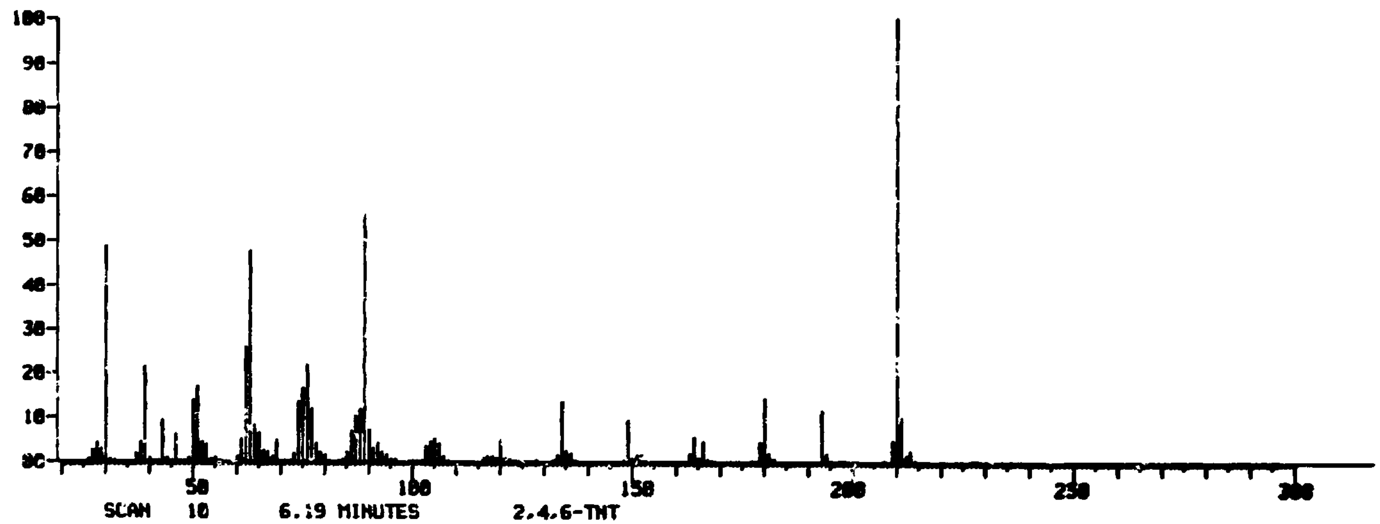
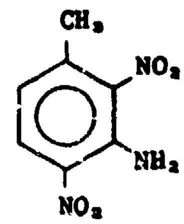
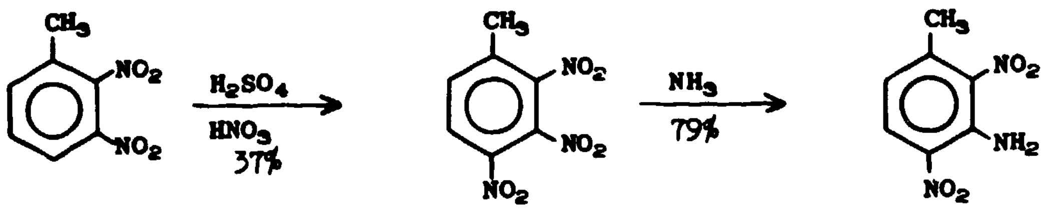


FIGURE 97 MASS SPECTRUM OF 2,4,6-TRINITROTOLUENE

4.16 3-Amino-2,4-Dinitrotoluene
3-Methyl-2,6-dinitrobenzenamine



Source: Synthesis, SRI



Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 2.9, 3.0 (N-H, 1° aromatic amines), 3.3 (C-H, aromatic), 3.4 (C-H, methyl), 6.2, 6.85 (C=C, ring), 6.4, 7.4 (N=O), 7.85 (C-N, 1° aromatic amines), 9.6, 13.3 (C-H), 11.2 (C-N, aromatic NO_2), 7.7, 8.55, 8.85, 11.9, 12.1, 12.95 μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.13 (singlet, 3H) CH_3; δ 6.50 (doublet, H, J = 8.5 cps) H_a

δ 7.30 (singlet, 2H) NH_2; δ 7.94 (doublet, H, J = 8.5 cps) H_b.

uv (Methanol)--λ_{max} = 226.2 nm, A = 1.494, ε = 21,700
λ_{max} = 268.0 nm, A = 0.484, ε = 7050
λ_{max} = 380.0 nm, A = 0.336, ε = 4890.

Purity (99.8%)

Elemental Analysis--

Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.65; H, 3.58; N, 21.31
Found: C, 42.40; H, 3.54, N, 21.16.

High-Pressure Liquid Chromatography--One major component (representing 99.75% of the total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow Rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 435 sec 3-amino-2,4-dinitrotoluene 99.75%; 78 sec impurity 0.25%.

Gas Chromatography--One major component (respresenting 99.76% of the total peak areas) and three minor components were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 110 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 1145 sec 3-amino-2,4-dinitrotoluene 99.76%; 276 sec impurity 0.03%; 427 sec impurity 0.06%; 973 sec impurity 0.15%.

Elemental Analysis--

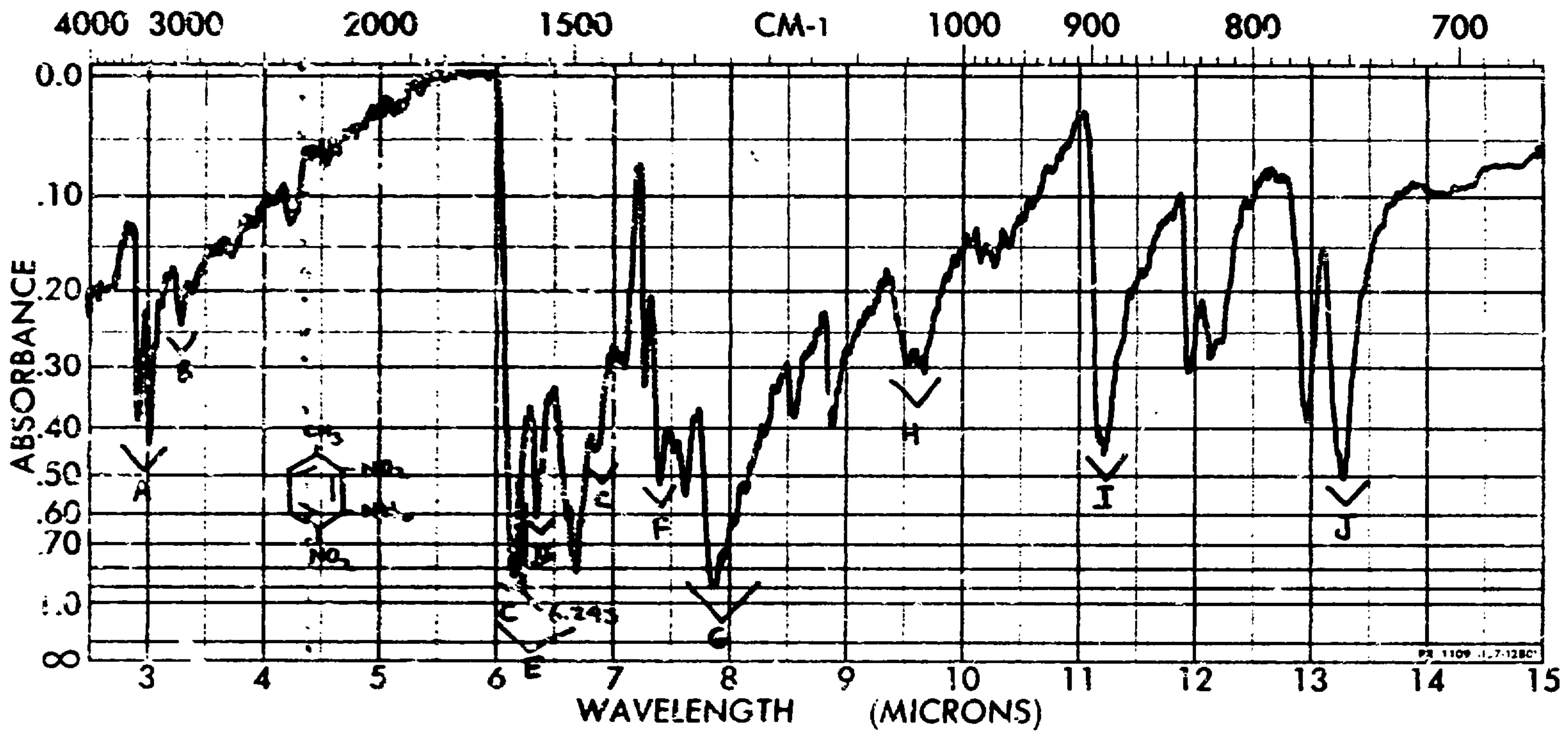
Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.65; H, 3.58; N, 21.3[illegible]
Found: C, 42.40; H, 3.54, N, 2[illegible].

High-Pressure Liquid Chromatography--One major component (representing 99.75% of the total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow Rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 435 sec 3-amino-2,4-dinitrotoluene 99.75%; 78 sec impurity 0.25%.

Gas Chromatography--One major component (respresenting 99.76% of the total peak areas) and three minor components were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromosorb W-HP 80/1[illegible]
- Temperature: 110 to 220 at 4°/min.
- Flow rate: 30 ml/min [illegible]
- Detection: Flame ionization.
- Retention time: 11[illegible] sec 3-amino-2,4-dinitrotoluene 99.76%; 276 sec impurity 0[illegible]; 427 sec impurity 0.06%; 973 sec impurity 0.15%.



SPECTRUM NO. 11	ORIGIN	LEGEND A: N-H stretch 1° Aromatic amines.	REMARKS
SAMPLE 3-AMINO-2,4-DINITROTOLUENE		1. B: Aromatic C-H stretch.	F: N=O stretch – symmetric
KBr PELLET	PURITY	C: C=C Ring stretch.	G: C-N stretch – 1° aromatic amines
		2. D: N=O stretch asymmetric.	
I.D. 258.9 g	PHASE	E: N-H Bend	H: In plane C-H bend.
		DATE JUNE 20, 1977	I. Ar-NO2 C-N stretch
	THICKNESS	OPERATOR C. INGERSOLL	J. Out of plane C-H BEND.

SPECTRUM NO. 25
SAMPLE

FIGURE 93 INFRARED SPECTRUM OF 3-AMINO-2,4-DINITROTOLUENE

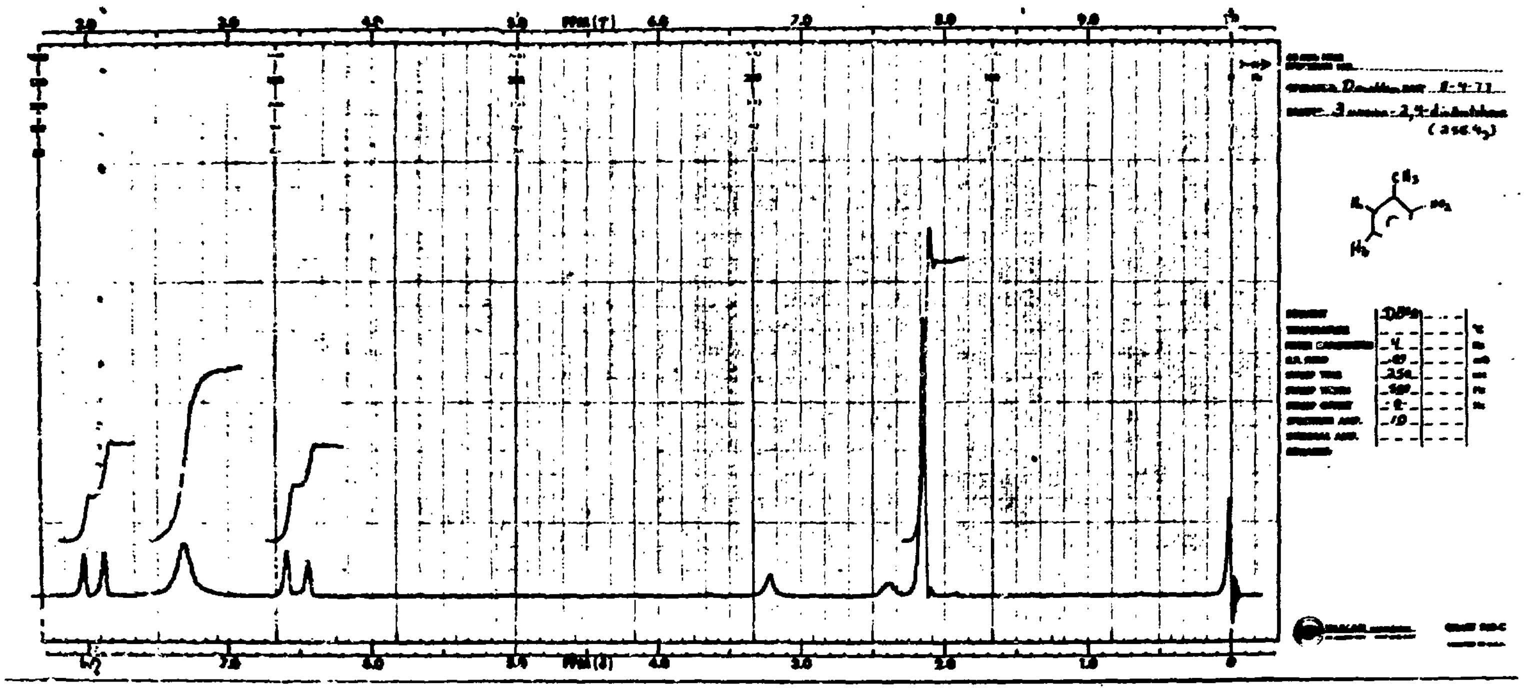
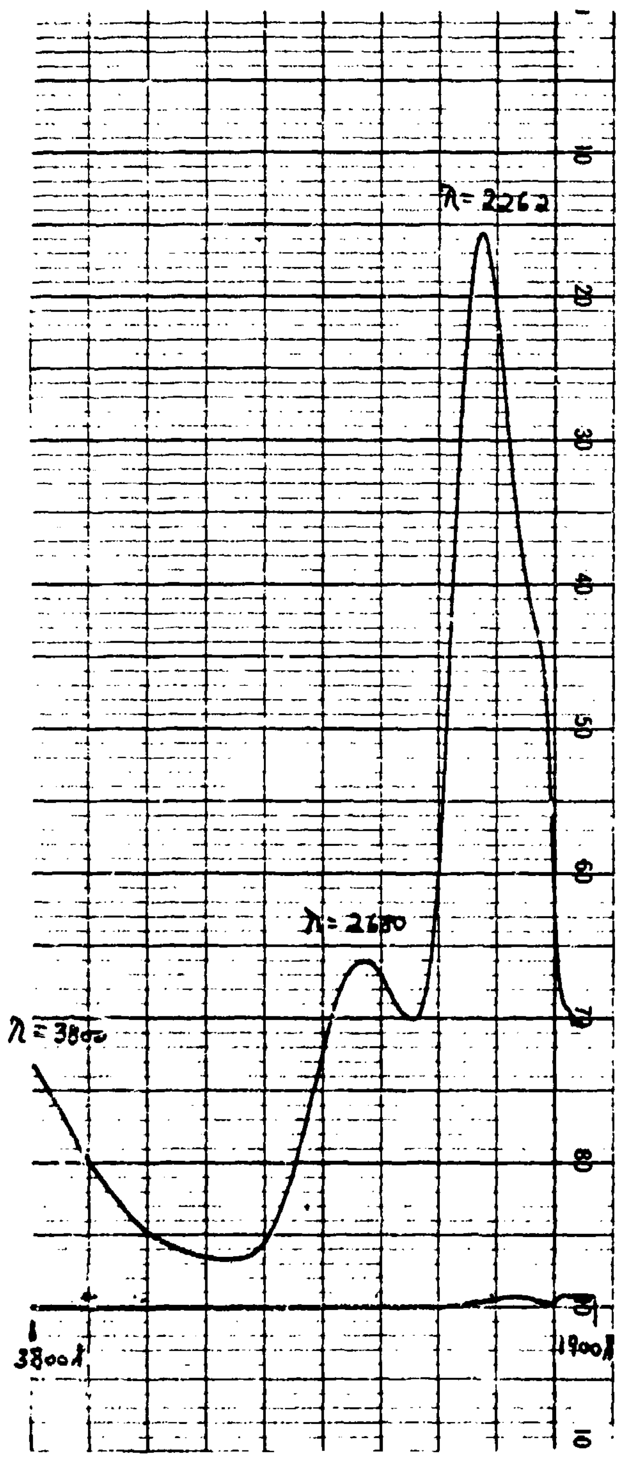


FIGURE 99 NMR SPECTRUM OF 3-AMINO-2,4-DINITROTOLUENE



3-amino-2,4-dinitrotoluene

$C = 6.87 \times 10^{-5}$ M/l

$A_{2262Å} = 1.494$
$\epsilon_{2262Å} = 21700$

$A_{2680Å} = .484$
$\epsilon_{2680Å} = 7050$

$A_{3800Å} = .336$
$\epsilon_{3800Å} = 4890$

FIGURE 100 UV SPECTRUM OF 3-AMINO-2,4-DINITROTOLUENE

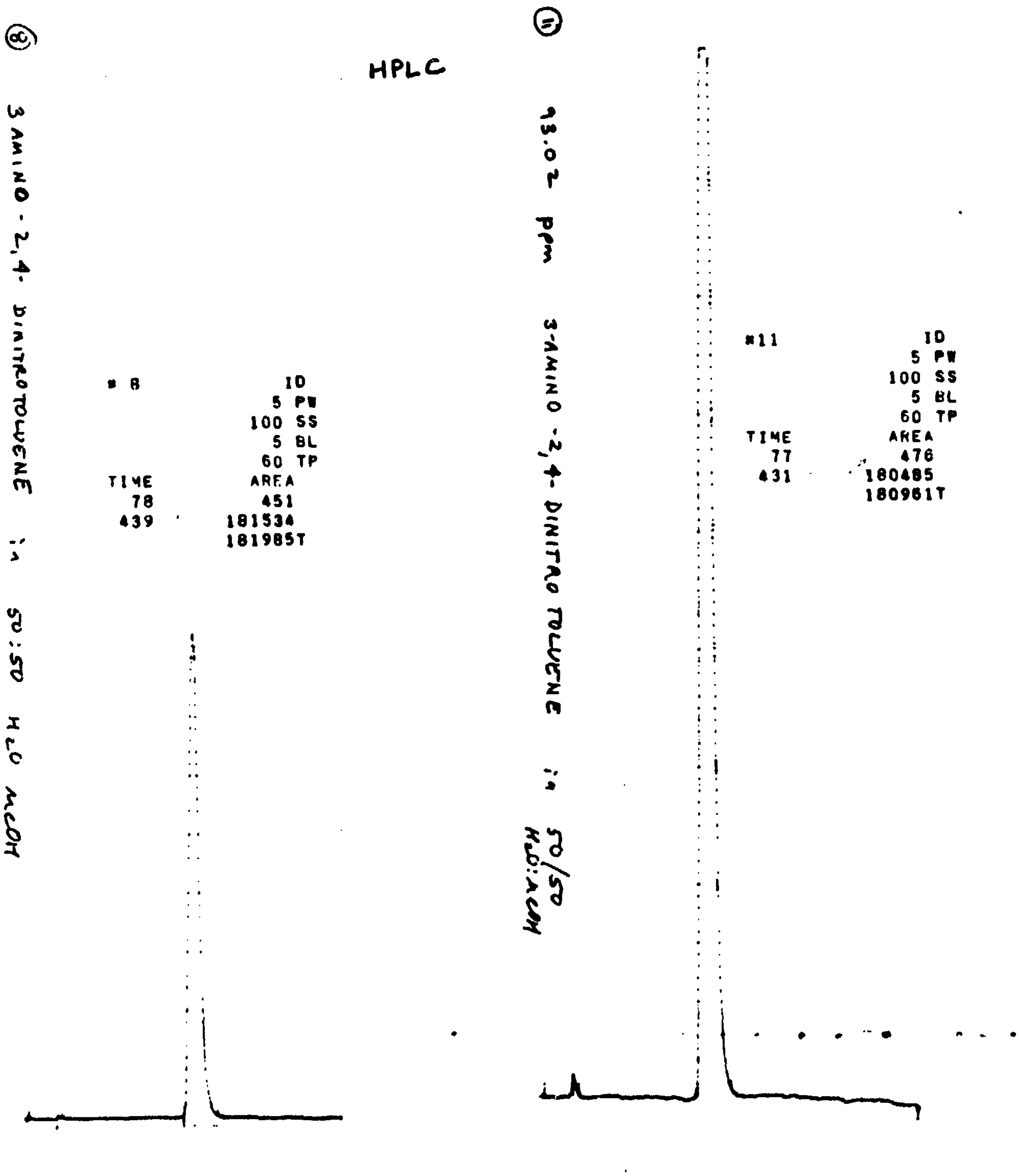


FIGURE 101 HPLC CHROMATOGRAM OF 3-AMINO-2,4-DINITROTOLUENE

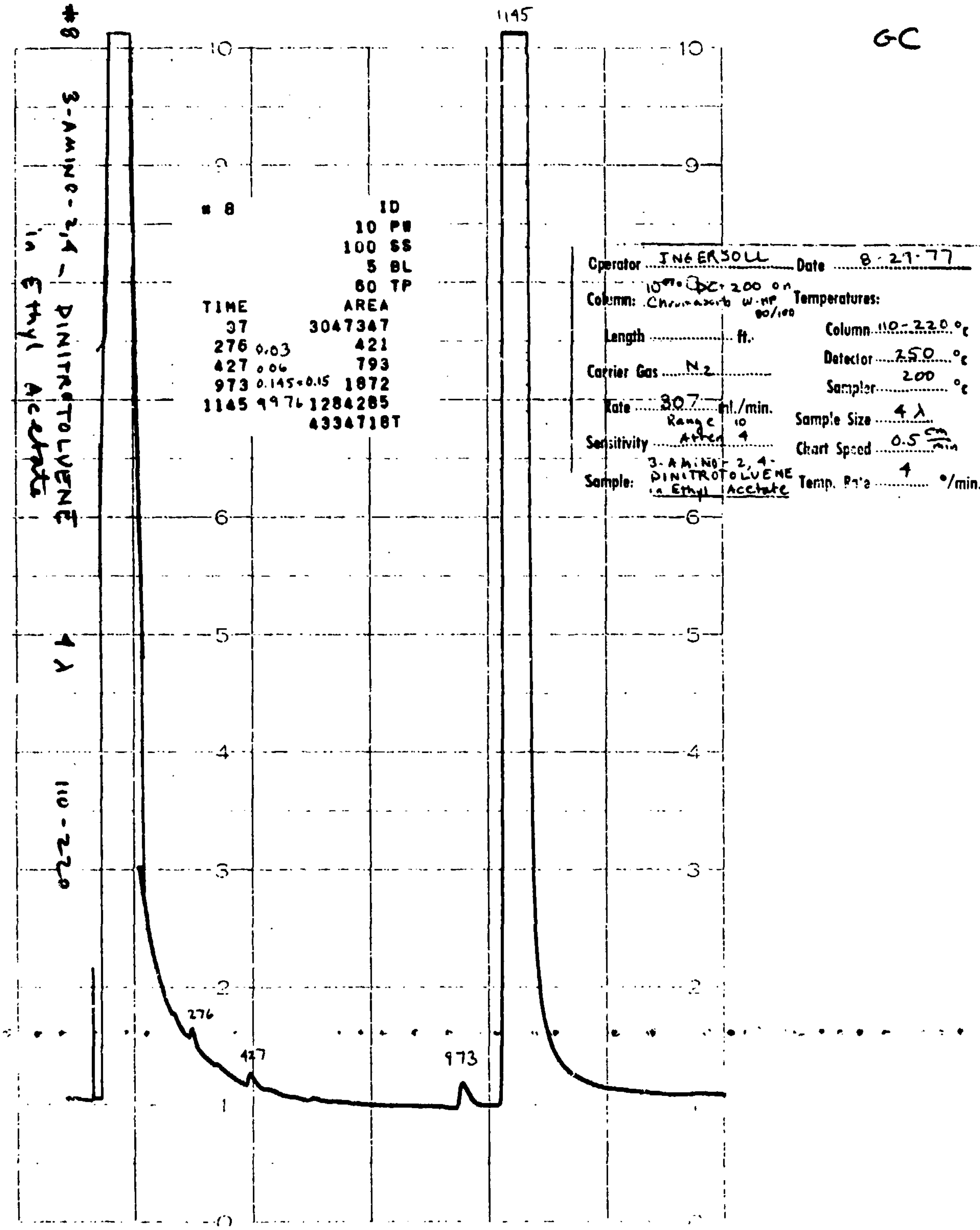


FIGURE 102 GC SPECTRUM OF 3-AMINO-2,4-DINITROTOLUENE

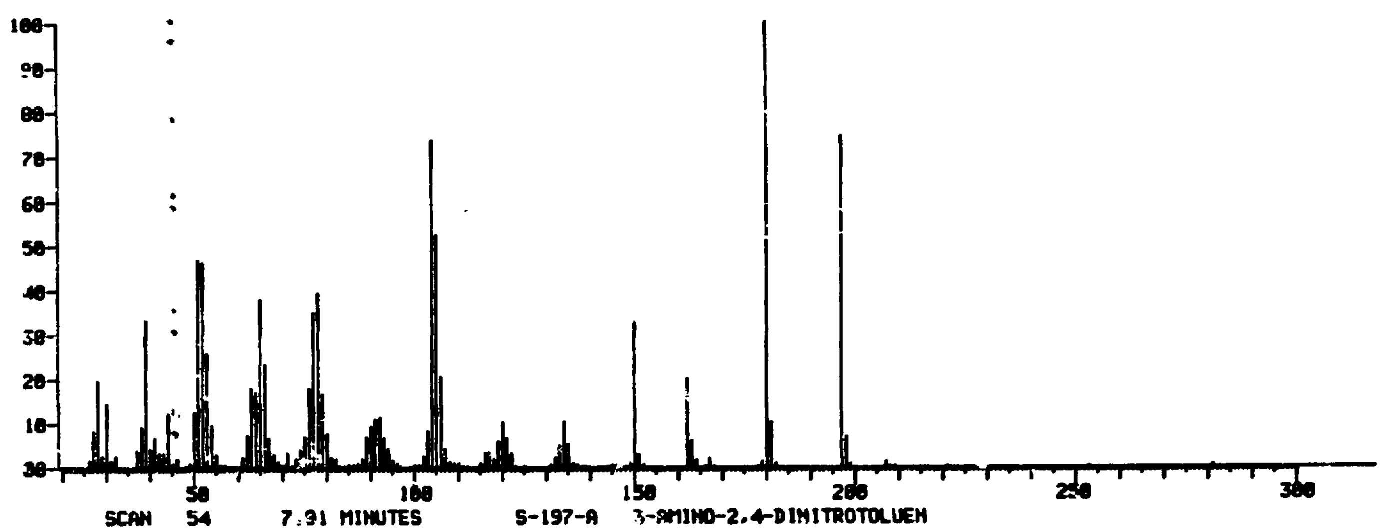
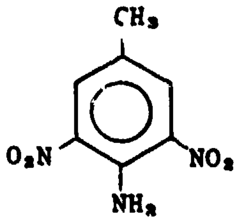
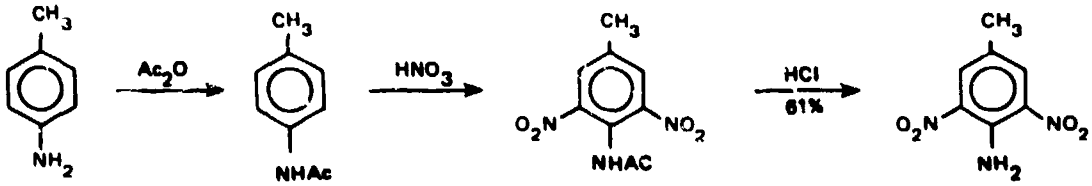


FIGURE 103 MASS SPECTRUM OF 3-AMINO-2,4-DINITROTOLUENE

4.17 4-Amino-3,5-Dinitrotoluene
4-Methyl-2,6-dinitrobenzenamine
[6393-42-6]



Source: Synthesis, SRI



Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed:

(1) (KBr pellet) 2.9, 3.0 (N-H, 1° aromatic amines), 6.15, 6.95 (C=C, ring), 6.5, 7.4 (N=O), 8.0 (C-N, 1° aromatic amines), 11.2 (C-N, aromatic NO_2), 13.65 (C-H), 12.55, 12.95 µm.

(2) (KBr pellet) 5-6 (aromatic overtones) µm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.20 (singlet, 3H) CH_3; δ 8.10 (singlet, 2H) NH_2;
δ 8.22 (singlet, 2H) H.

Peaks at 2.4 and 3.2 are from DMSO and H_2O, respectively.

uv (Methanol)--λ_{max} = 225.0 nm, A = 0.414, ε = 18,300
λ_{max} = 252.0 nm, A = 0.189, ε = 8360.

Purity (97.35 ± 2.2%)

Elemental Analysis--

Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.6; H, 3.6; N, 21.3

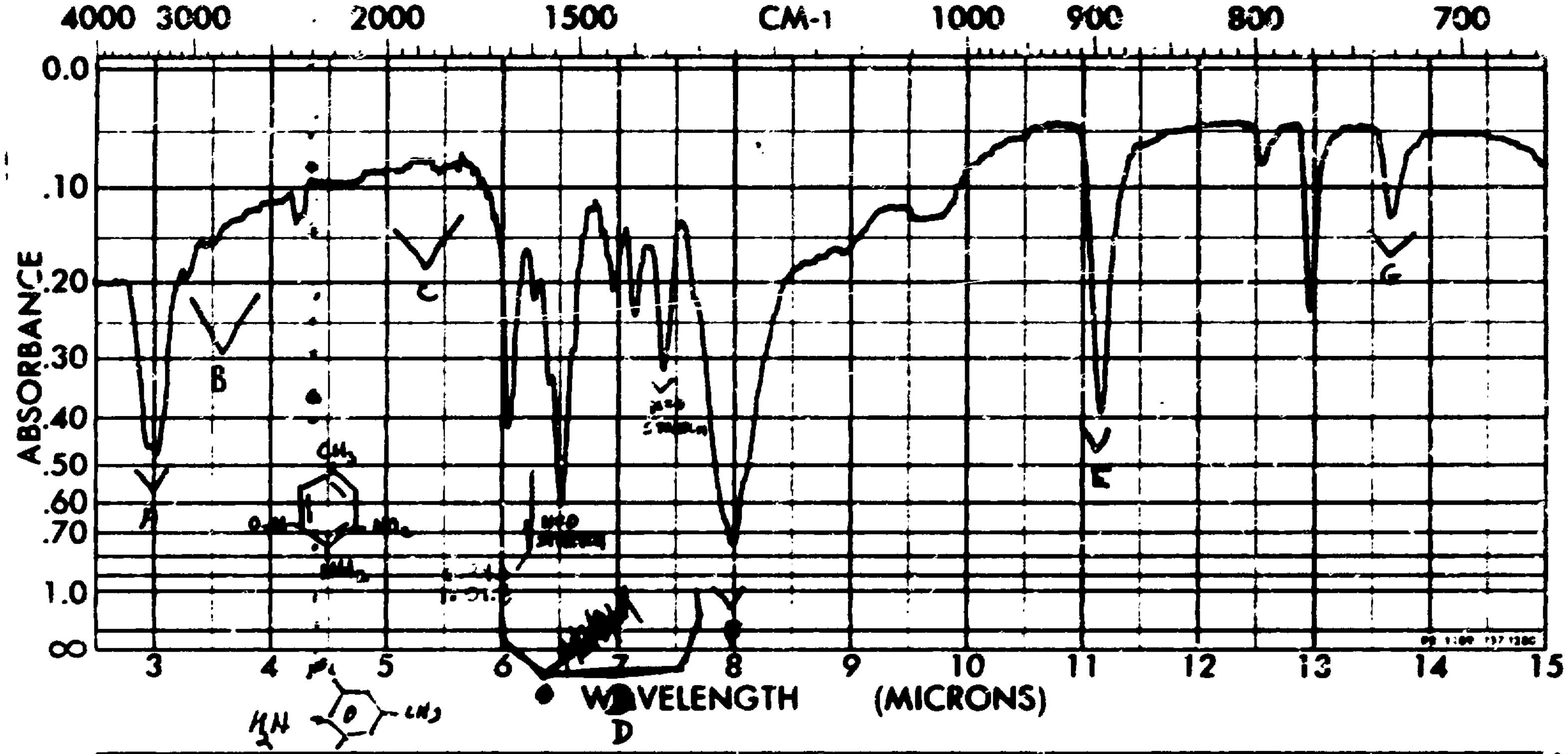
Found: C, 42.53; H, 3.51; N, 20.68.

High-Pressure Liquid Chromatography--One major component [representing 95.15% (avg.) of the total peak areas] and three minor components were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.).
- Solvent: 50% H_2O/50% CH_3OH.
- Flow rate: 1.6 ml/min.
- Detection: uv at 254 nm.
- Average retention time: 661 sec 4-amino-3,5-dinitrotoluene 95.15%; 74 sec impurity 0.37%; 226 sec impurity 3.98%; 266 sec impurity 0.50%.

Gas Chromatography--One major component (representing 99.55% of the total peak areas) and one minor component were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 110 to 220°C at 4°/min.
- Flow rate: 30 ml/min.
- Detection: Flame ionization.
- Retention time: 1214 sec 4-amino-3,5-dinitrotoluene 99.55%; 909 sec impurity 0.45%.



SPECTRUM NO. 12	ORIGIN	LEGEND	REMARKS SLOW SLIT = 1
SAMPLE 3,5-DINITRO-p-TOLUIDINE (4 AMINO-3,5-DINITROTOLUENE)		1.	A: N-H stretch 1° Aromatic Amine; B: No aromatic; C: No overtone (substitution)
KBr PELLET	PURITY	2.	D: C=C ring stretch; N-H; ArNO$_2$ N=O stretch asym.; ArNO$_2$ N=O stretch symm.
I.D.: Bottle #2	PHASE	DATE MAY 6, 1977	E: ArNO$_2$ C-N stretch
	THICKNESS	OPERATOR C. INGERSOLL	F: 1° ArNH$_2$ C-N; G: Out of plane C-H bend

SPECTRUM NO. 26
SAMPLE

FIGURE 104 INFRARED SPECTRUM OF 4-AMINO-3,5-DINITROTOLUENE

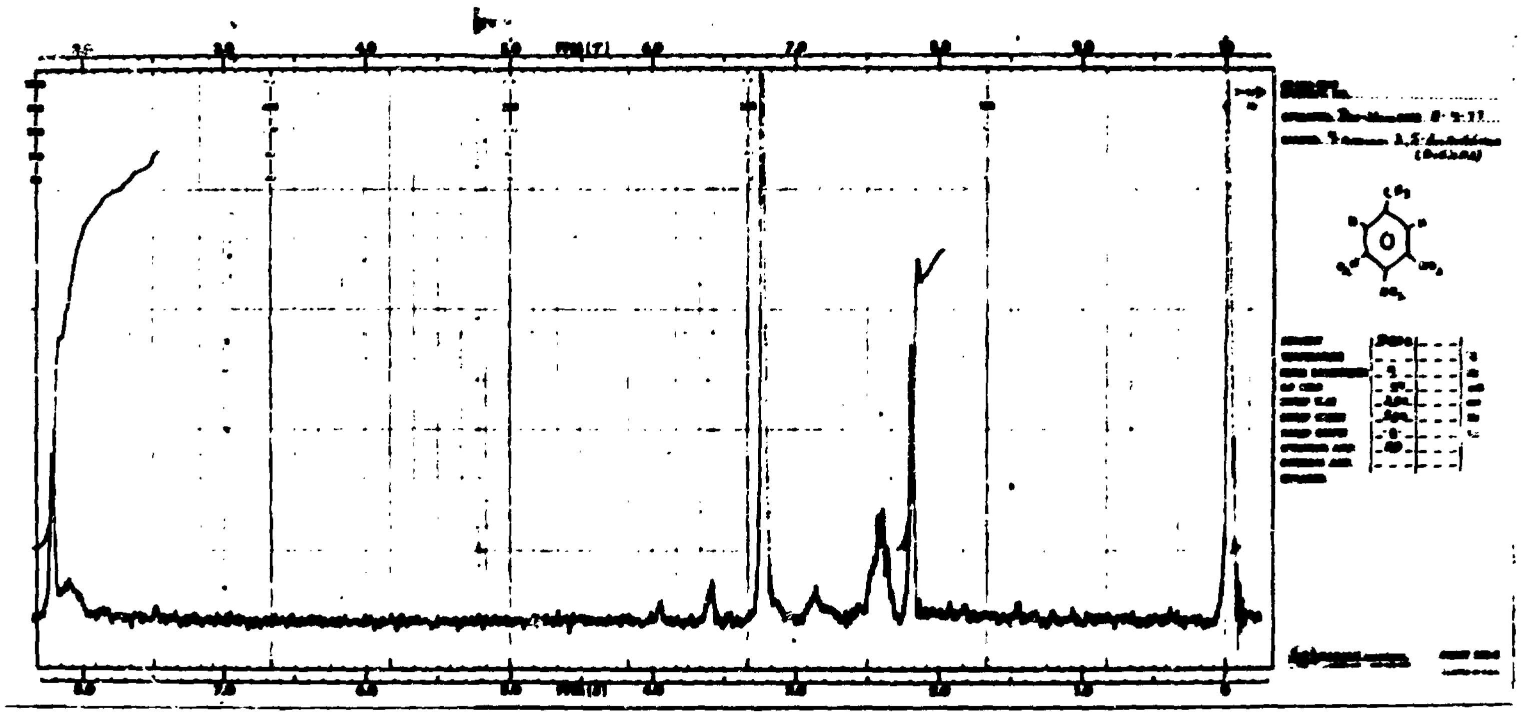


FIGURE 105 NMR SPECTRUM OF 4-AMINO-3,5-DINITROTOLUENE

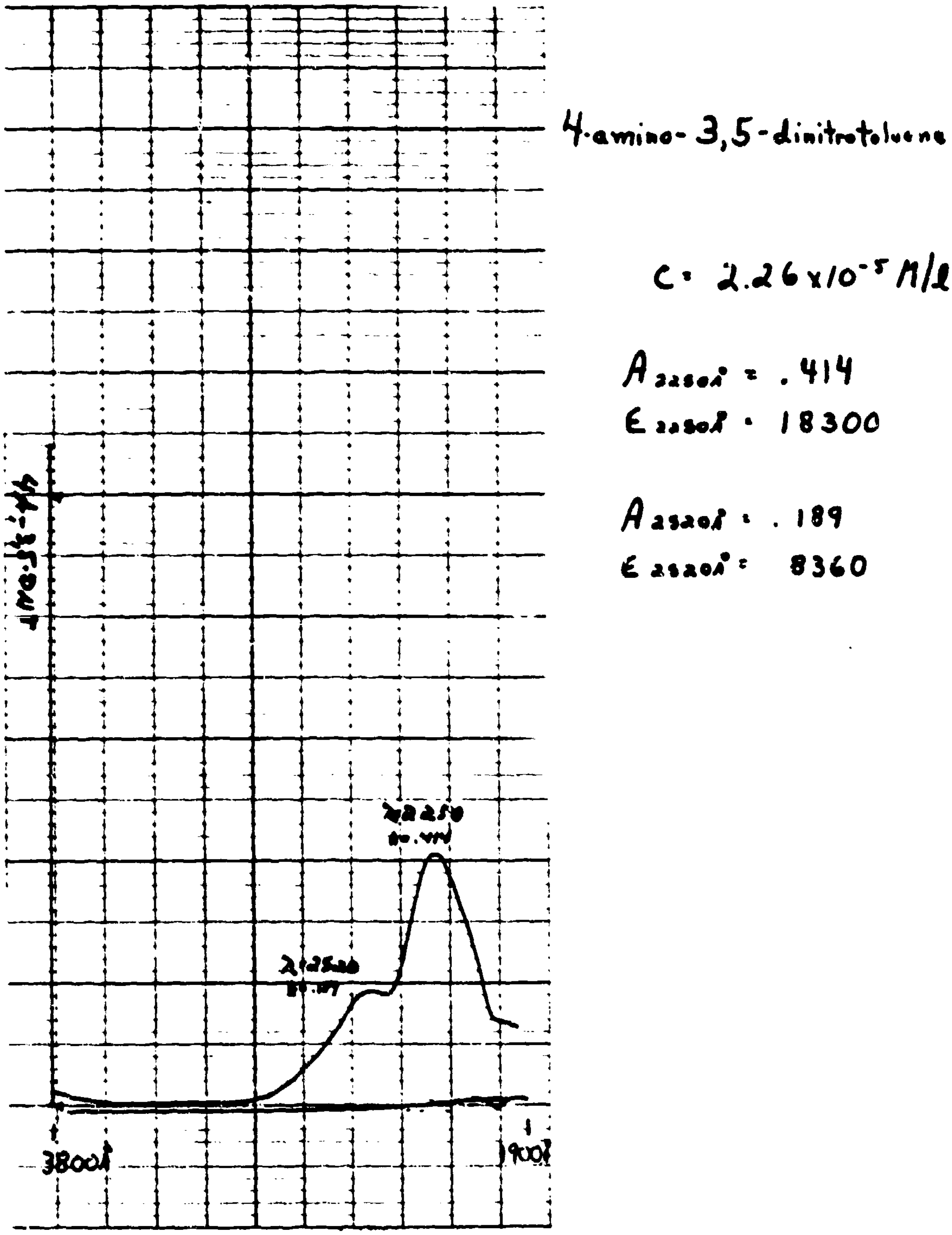


FIGURE 106 UV SPECTRUM OF 4-AMINO-3,5-DINITROTOLUENE

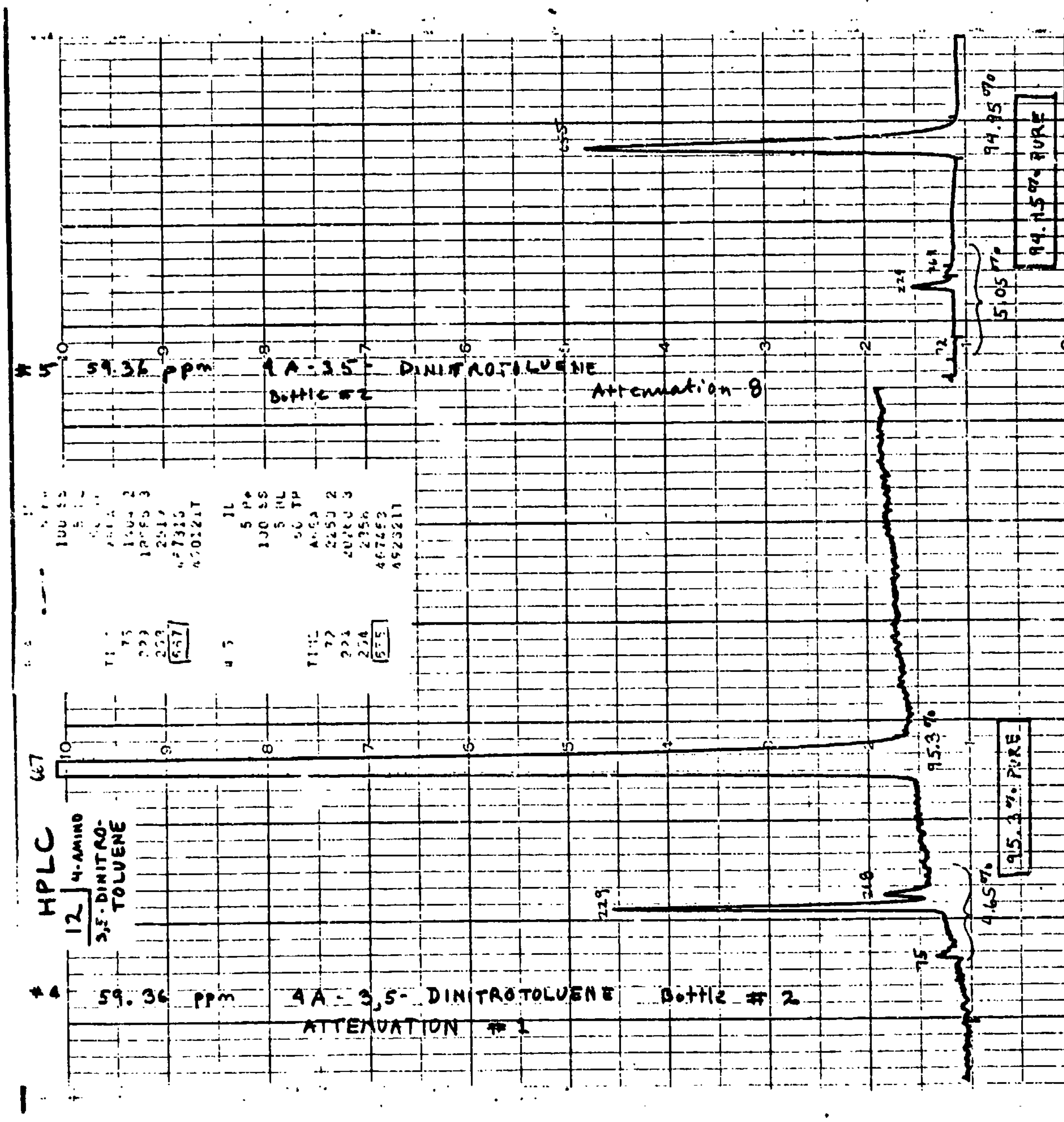


FIGURE 107 HPLC CHROMATOGRAM OF 4-AMINO-3,5-DINITROTOLUENE

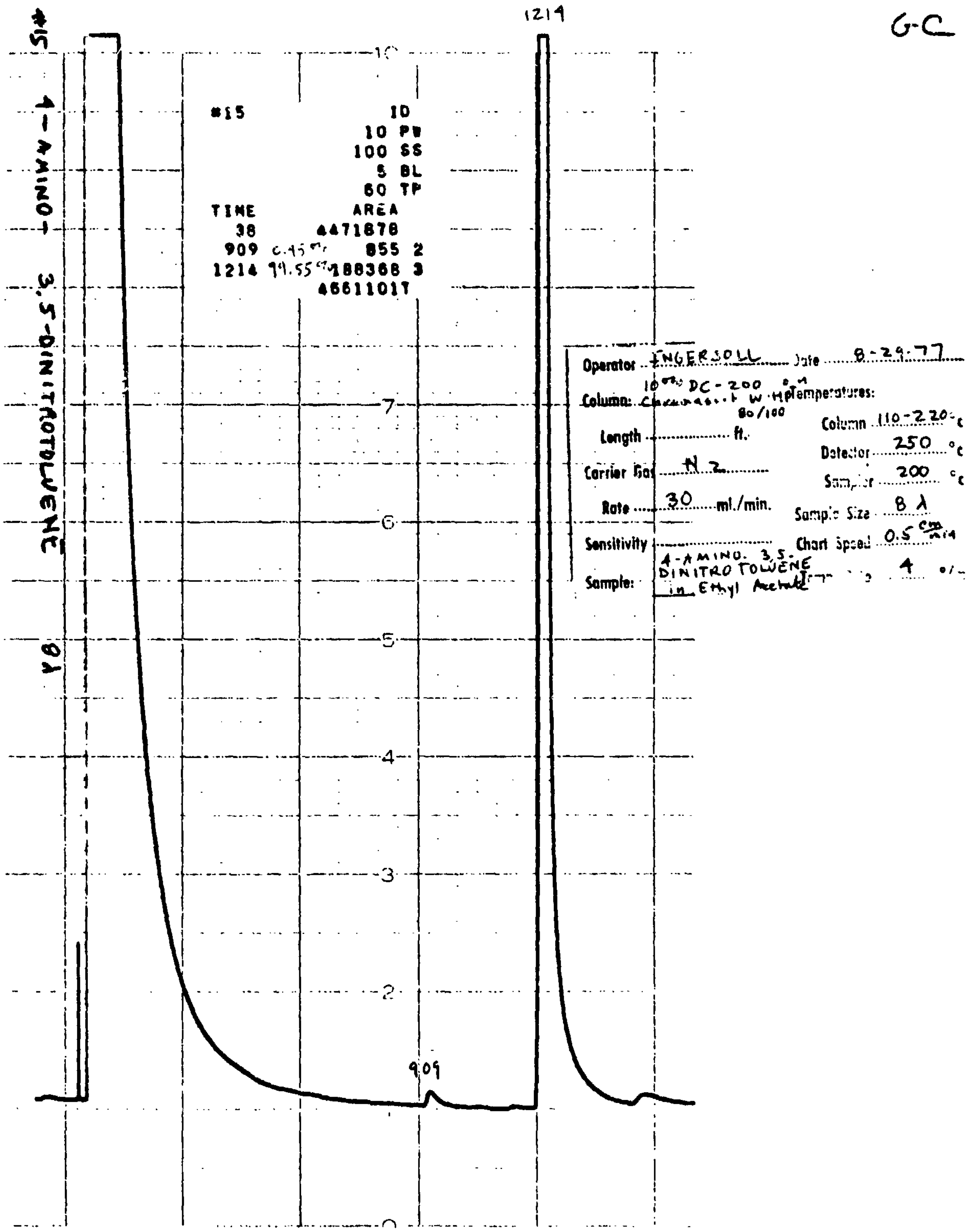


FIGURE 108 GC SPECTRUM OF 4-AMINO-3,5-DINITROTOLUENE

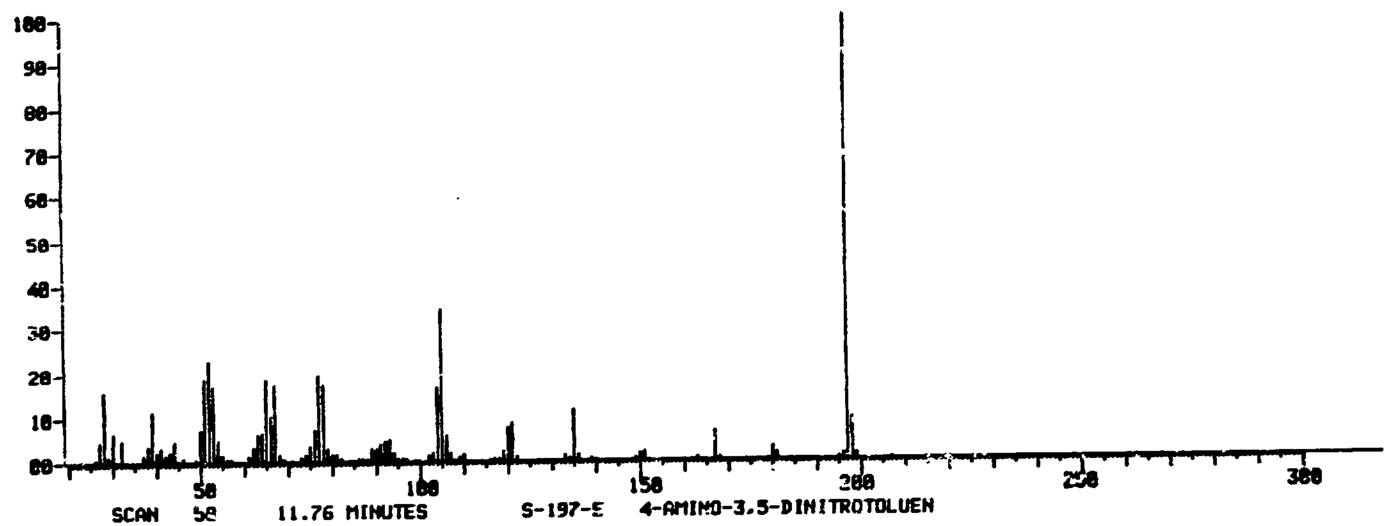
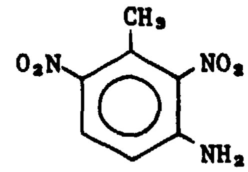
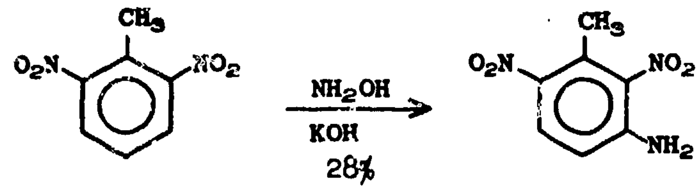


FIGURE 109 MASS SPECTRUM OF 4-AMINO-3,5-DINITROTOLUENE

4.18 <u>3-Amino-2,6-Dinitrotoluene</u>
3-Methyl-2,4-dinitrobenzenamine



Source: Synthesis, SRI



<u>Identity</u>

<u>Ir</u>--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet), 2.9, 3.0 (N-H, 1° aromatic amines), 5.5-59 (atmospheric H_2O), 6.2, 6.8 (C=C, ring), 6.5, 7.4 (N=O), 7.65 (C-N, 1° aromatic amines), 11.2 (C-N, aromatic NO_2), 12.15, 12.9, 13.25, 14.4 μm.

<u>Nmr</u>--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed and the number of protons each signal represents was determined from signal integrals:

δ 2.27 (singlet, 3H) CH_3; δ 3.17 (singlet, H) H_a
δ 6.72 (doublet, 2H, J = 10 cps) NH_2
δ 7.85 (doublet, H, J = 10 cps) H_b.

<u>uv (Methanol)</u>--λ_{max} = 205.4 nm, A = 0.496, ε = 14,900
λ_{max} = 225.0 nm, A = 0.373, ε = 11,200
λ_{max} = 343.0 nm, A = 0.333, ε = 9970.

<u>Purity</u> (99.85%)

Elemental Analysis--

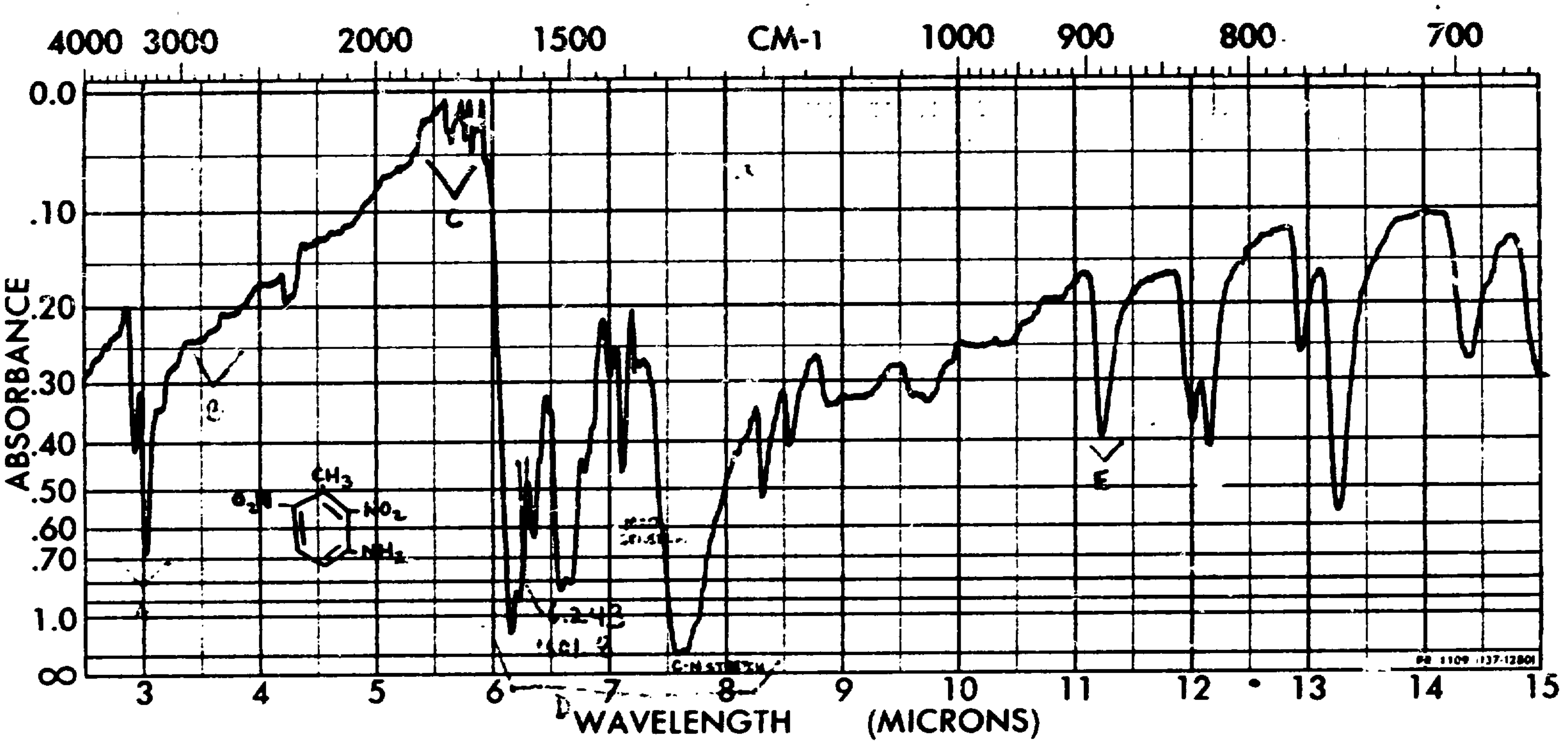
Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.65; H, 3.58; N, 21.31
Found: C, 42.41; H, 3.50; N, 21.14.

High-Pressure Liquid Chromatography--One major component (representing 99.8% of the total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 538 sec 3-amino-2,6-dinitrotoluene 99.8%; 150 sec impurity 0.2%.

Gas Chromatography--One major component (representing 99.9% of the total peak areas) and one minor component were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 110 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 1491 sec 3-amino-2,6-dinitrotoluene 99.9%; 755 sec impurity 0.1%.



SPECTRUM NO. 13	ORIGIN	LEGEND A: N-H stretch B: Ar aromatic C-H C: Atmospheric H2O D: C=C ring stretch; NH; C-N 2. 6.5 μm: ArNO2 N=O stretch 7.4 μm: ArNO2 N=O stretch	1° Aromatic Amine REMARKS SLOW SLIT 1 asymmetric symmetric
SAMPLE 3-AMINO-2,6-DINITROTOLUENE KBr PELLET	PURITY		
I.D. 8149-87-2	PHASE	DATE MAY 6, 1977	E: ArNO2 C-N stretch
recrystallized m.p. 125-130	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO. 28
SAMPLE

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK

FIGURE 110 INFRARED SPECTRUM OF 3-AMINO-2,6-DINITROTOLUENE

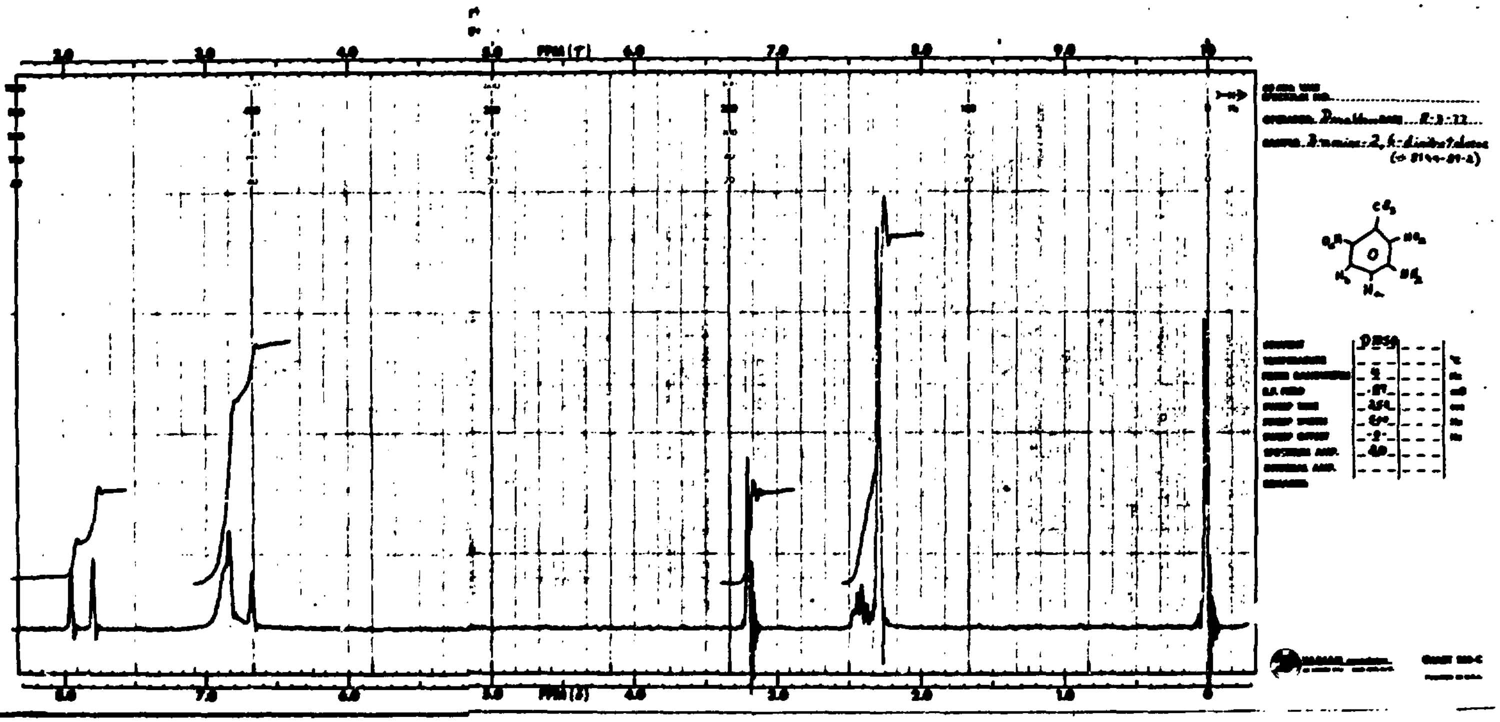
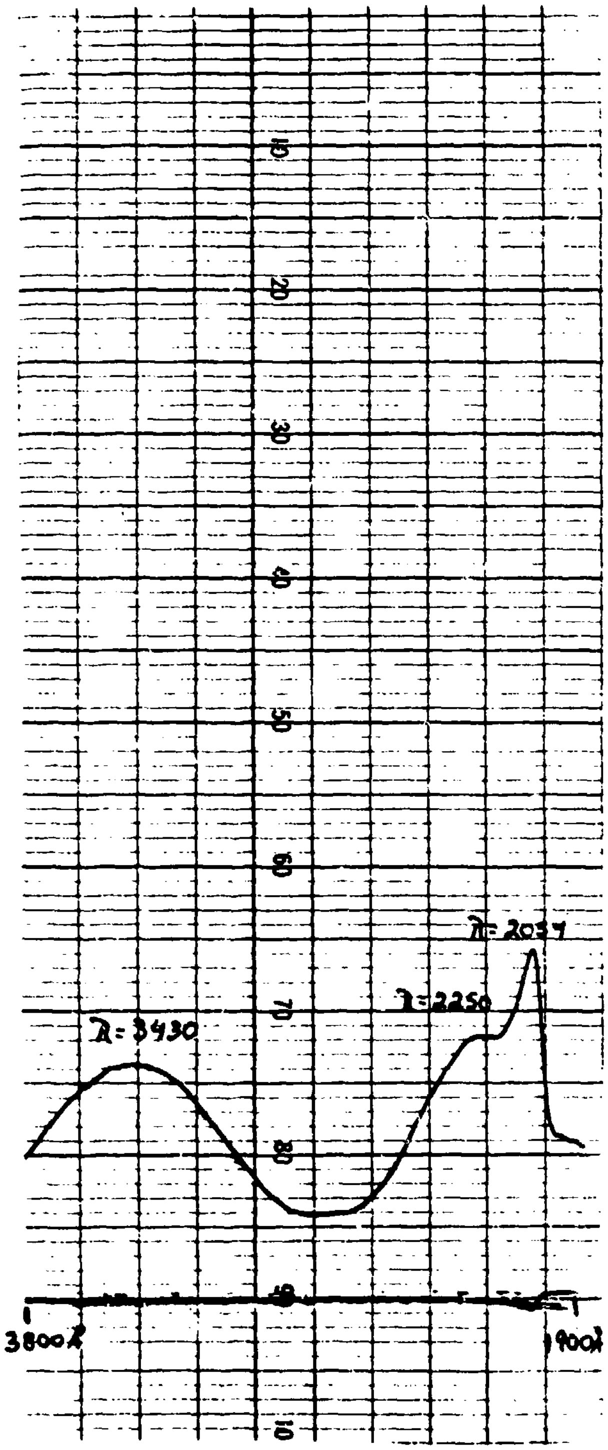


FIGURE 111 NMR SPECTRUM OF 3-AMINO-2,6-DINITROTOLUENE



3-amino-2,6-dinitrotoluene

$C = 3.34 \times 10^{-5}$ M/l

$A_{2054Å} = .496$

$\epsilon_{2054Å} = 14900$

$A_{2250Å} = .373$

$\epsilon_{2250Å} = 11200$

$A_{3430Å} = .333$

$\epsilon_{3430Å} = 9970$

FIGURE 112 UV SPECTRUM OF 3-AMINO-2,6-DINITROTOLUENE

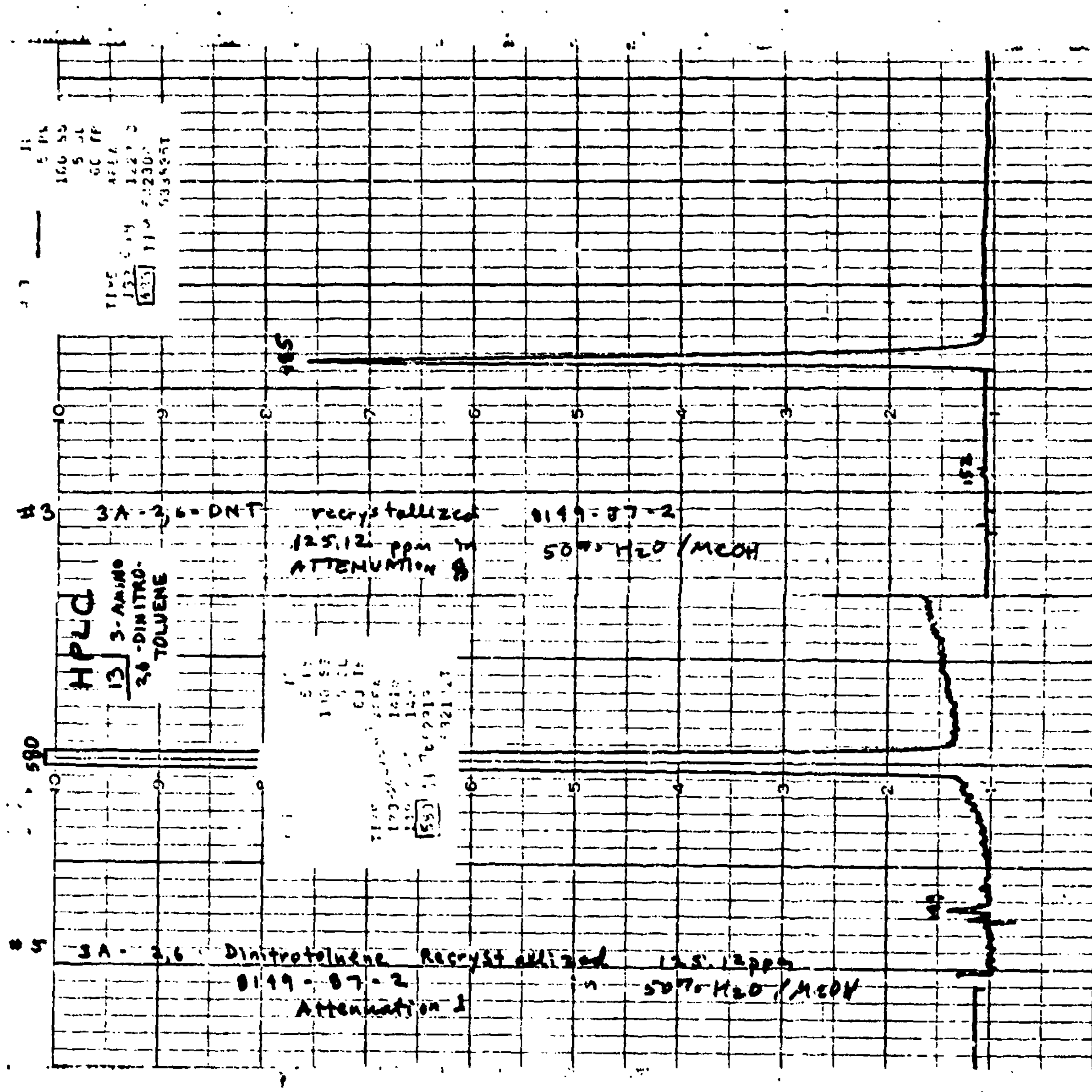


FIGURE 113 HPLC CHROMATOGRAM OF 3-AMINO-2,6-DINITROTOLUENE

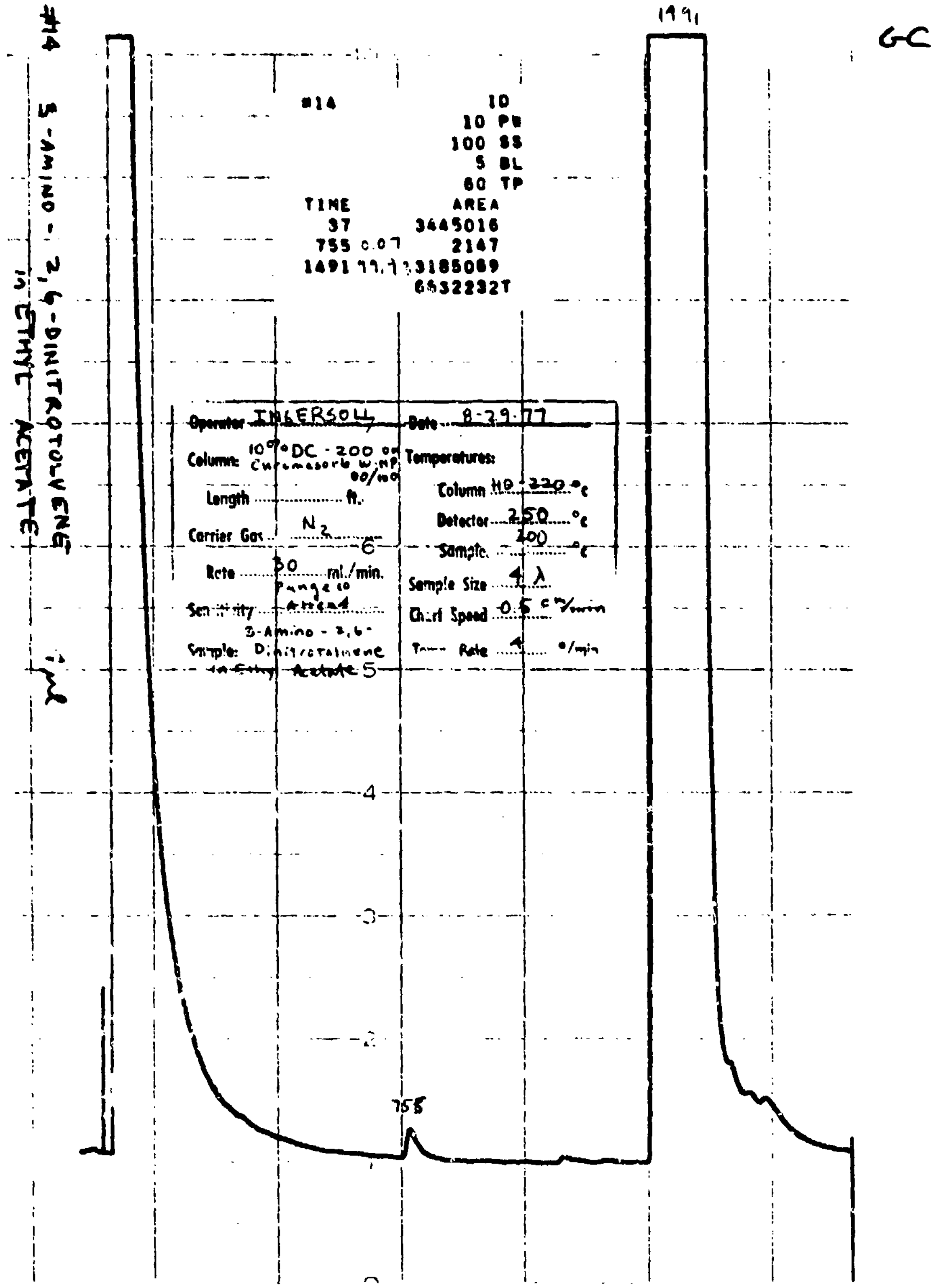


FIGURE 114 GC SPECTRUM OF 3-AMINO-2,6-DINITROTOLUENE

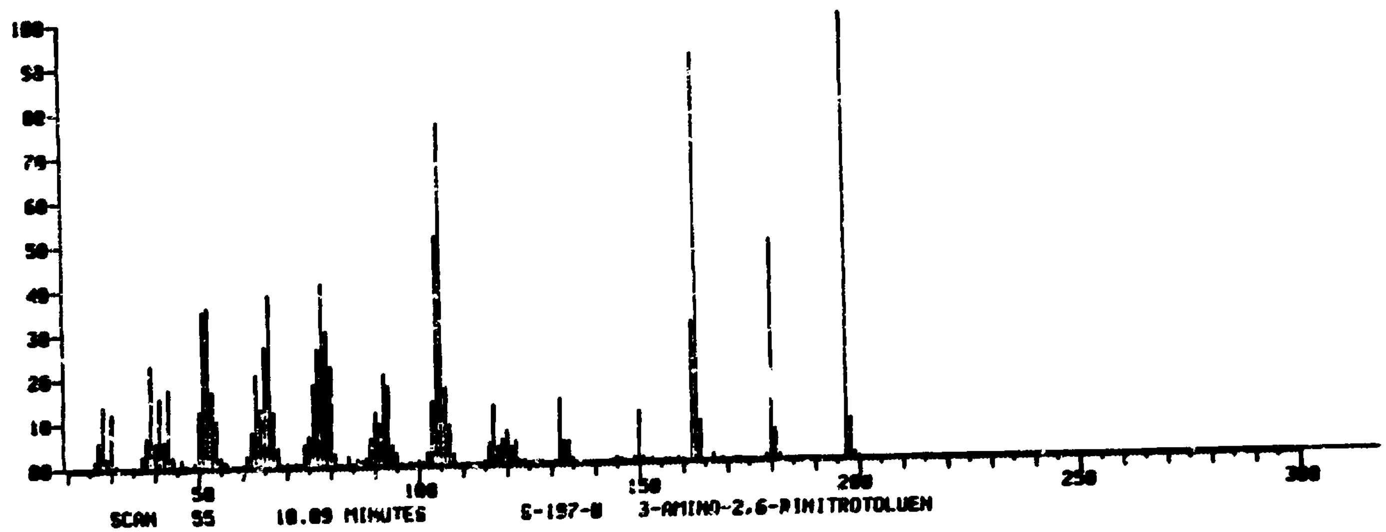
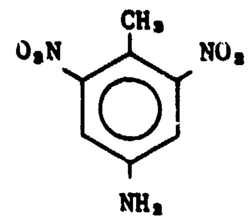


FIGURE 115 MASS SPECTRUM OF 3-AMINO-2,6-DINITROTOLUENE

4.19 <u>4-Amino-2,6-Dinitrotoluene</u>
4-Methyl-3,5-dinitrobenzenamine
[1946-51-0]



Source: Naval Surface Weapons Center (obtained from Aldrich Chemical Co. under Navy Contract N60921-75-C-0251, September 1976)

<u>Identity</u>

<u>Ir</u>--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 2.9, 3.0 (N-H, 1° aromatic amines), 3.3 (=C-H, aromatic), 6.1, 6.7 (C=C, ring), 6.5, 7.4 (N=O), 7.65 (C-N, 1° aromatic amines), 13.65 (N-H), 7.0, 7.2, 8.3, 11.05, 12.3, 12.85, 13.4 µm.

<u>Nmr</u>--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.12 (singlet, 3H) CH_3; δ 6.00 (singlet, 2H) NH_2
δ 7.20 (singlet, 2H) H.

<u>uv (Methanol)</u>--λ_{max} = 205.0 nm, A = 0.360; ε = 17,800
λ_{max} = 234.8 nm, A = 0.505; ε = 20,500.

<u>Purity</u> (99.7 ± 0.3%)

<u>Elemental Analysis</u>--

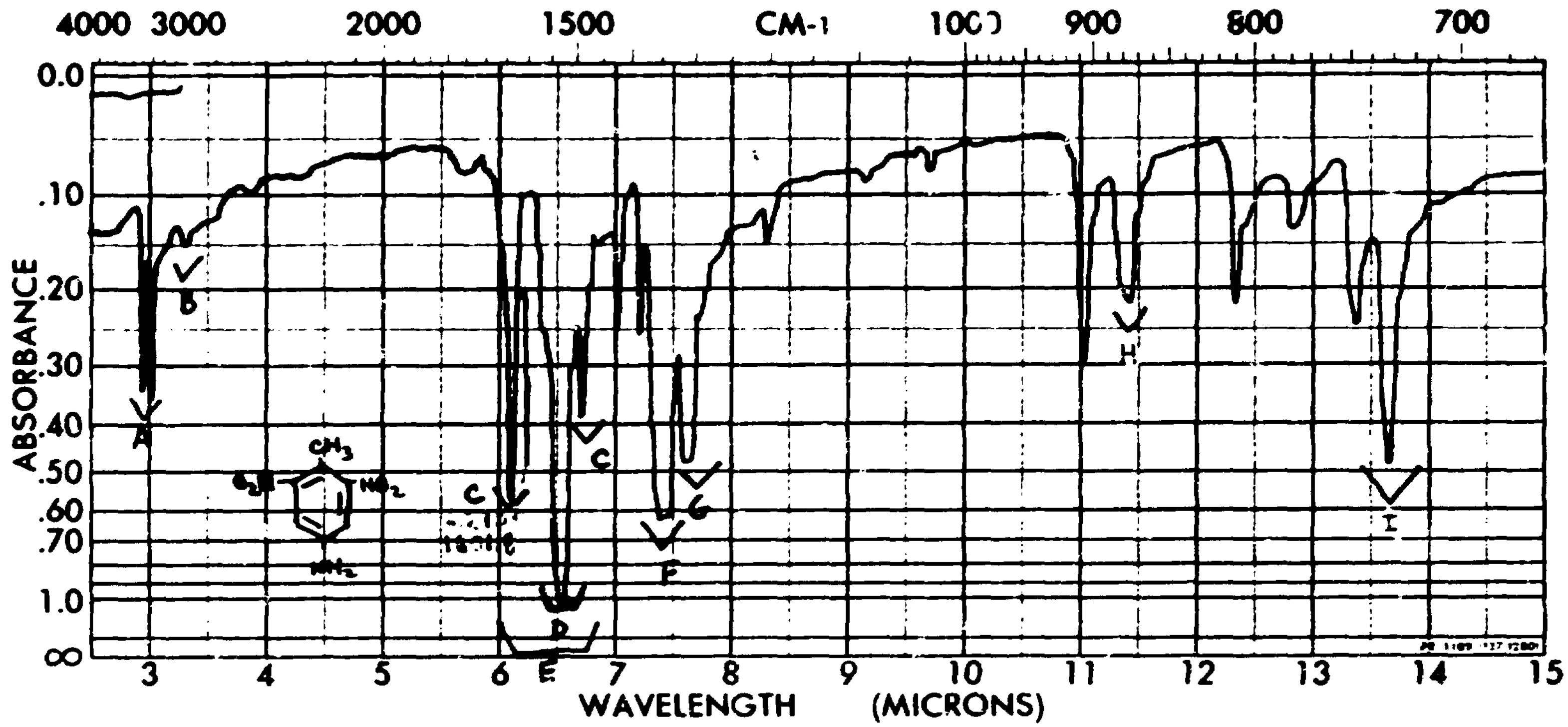
Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.6; H, 3 .3
Found: C, 42.52; H, .37.

<u>High-Pressure Liquid Chromatography</u> senting 100% of the total peak areas) was observed by hplc. following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 528 sec 4-amino-2,6-dinitrotoluene 100%.

Gas Chromatography--One major component (representing 99.4% of the total areas) and one minor component were observed by gc under the following conditions:

- Column: 5' ×4 mm glass column packed with DC-200 on Chromasorb W-HP 80/100.
- Temperature: 160 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 757 sec 4-amino-2,6-dinitrotoluene 99.4%; 863 sec impurity 0.6%.



SPECTRUM NO. 14

SAMPLE 4-AMINO-2,6-DINITROTOLUENE (KBr PELLET)

LOT SRI # 3

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND A: N-H stretch 1° Aromatic Amine
1. B: Aromatic C-H stretch
C: C=C ring stretch
2. D: NO_2 stretch asymmetric
E: N-H bend

DATE MAY 3, 1977

OPERATOR C. INGERSOLL

REMARKS
SCAN SPEED: SLOW

REFERENCE BEAM: Partially blocked with cardboard

F: N=O stretch symmetric
H: $Ar-NO_2$ C-N stretch
G: C-N stretch 1° aromatic amine
I: ~~N-H wag - out of plane~~ O-H bend

SPECTRUM NO. 31
SAMPLE

FIGURE 116 INFRARED SPECTRUM OF 4-AMINO-2,6-DINITROTOLUENE

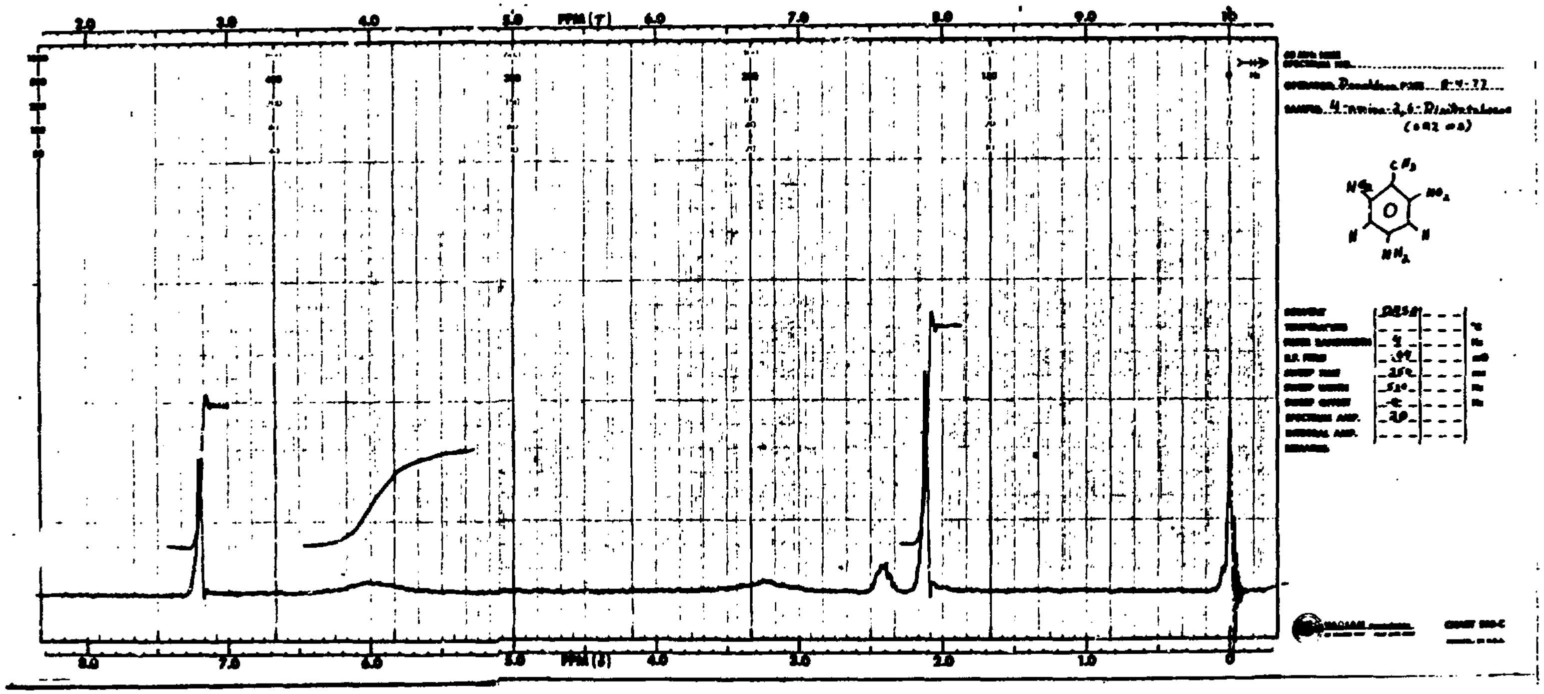
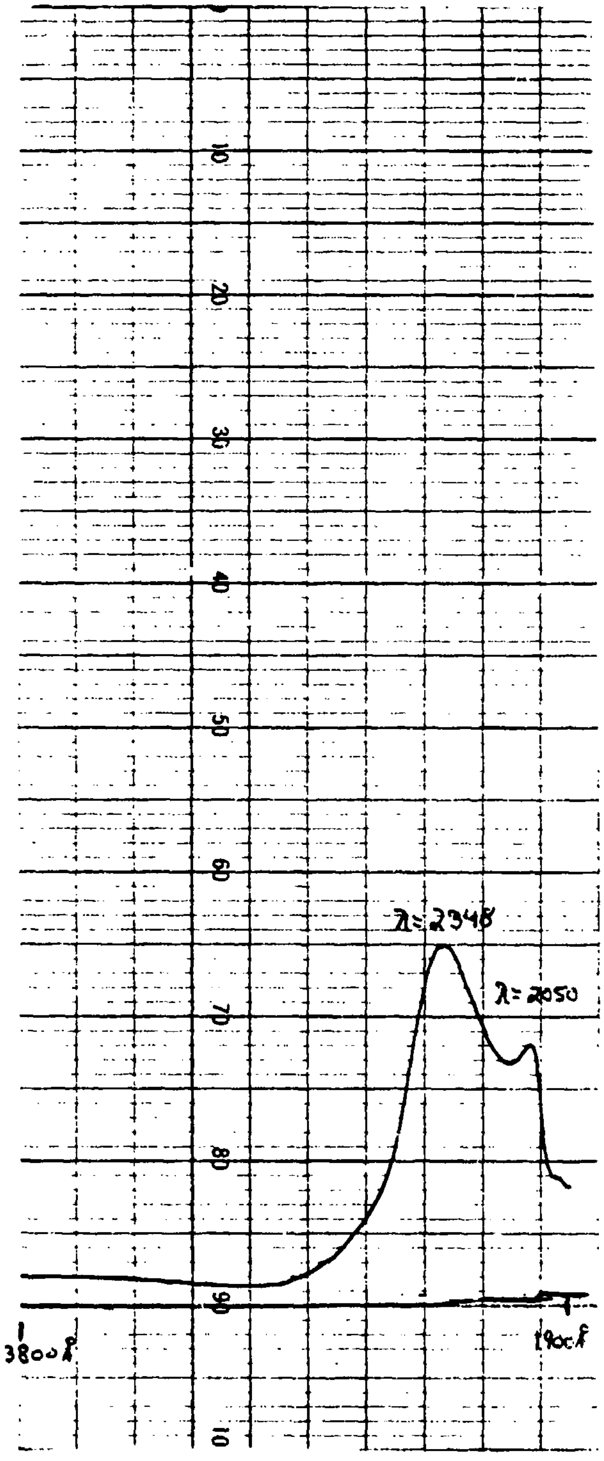


FIGURE 117 NMR SPECTRUM OF 4-AMINO-2,6-DINITROTOLUENE



4-amino-2,6-dinitrotoluene

$C = 2.02 \times 10^{-5}$ M/l

$A_{2050Å} = .360$

$\epsilon_{2050Å} = 17800$

$A_{2348Å} = .505$

$\epsilon_{2348Å} = 20500$

FIGURE 118 UV SPECTRUM OF 4-AMINO-2,6-DINITROTOLUENE

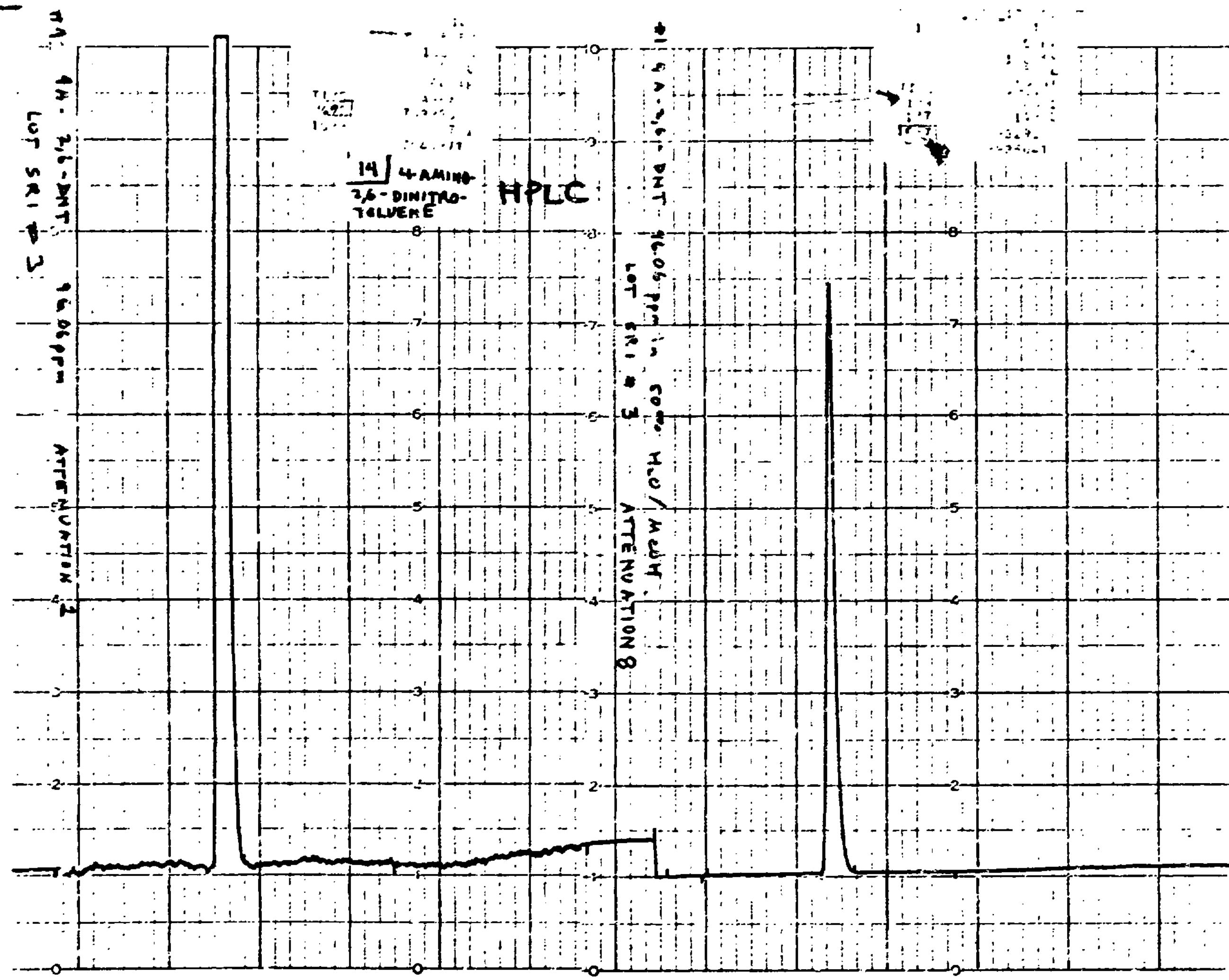


FIGURE 119 HPLC CHROMATOGRAM OF 4-AMINO-2,6-DINITROTOLUENE

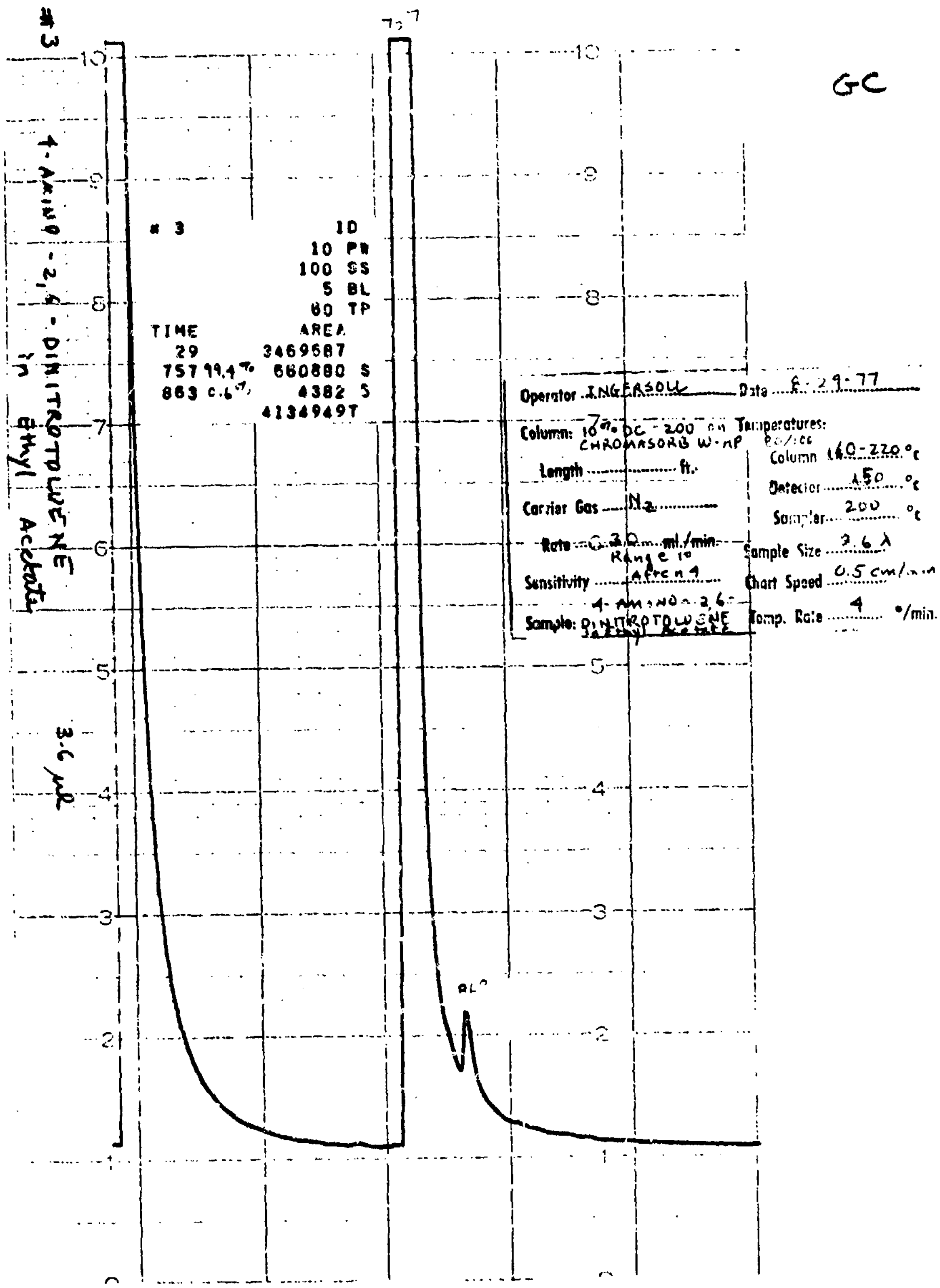


FIGURE 120 GC SPECTRUM OF 4-AMINO-2,6-DINITROTOLUENE

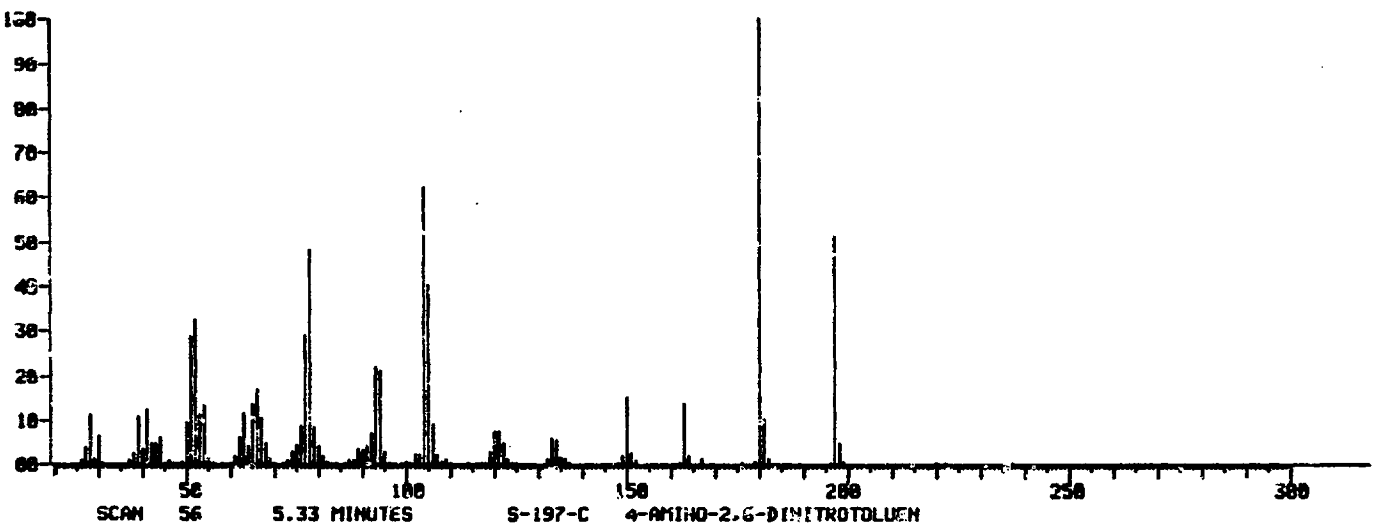
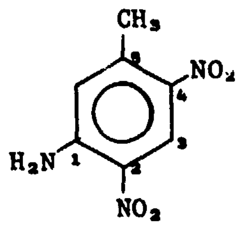
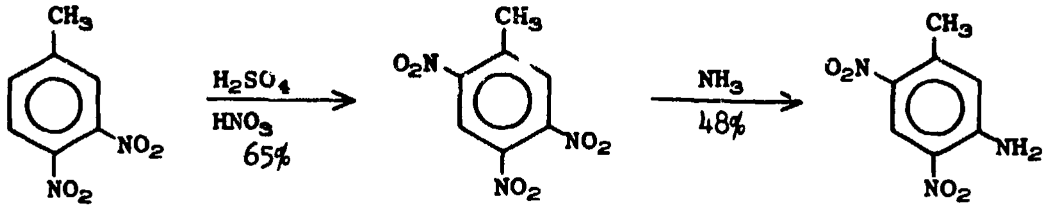


FIGURE 121 MASS SPECTRUM OF 4-AMINO-2,6-DINITROTOLUENE

4.20 <u>5-Amino-2,4-Dinitrotoluene (Recrystallized)</u>
5-Methyl-2,4-dinitrobenzenamine



Source: Synthesis, SRI



<u>Identity</u>

<u>Ir</u>--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 2.9, 3.0 (N-H, 1° aromatic amines), 6.2, 6.75 (C=C, ring), 6.4, 7.5 (N=O), 7.9 (C-N, 1° aromatic amines), 9.7, 13.5 (C-H), 11.5 (C-N, aromatic NO_2), 7.05, 8.5, 10.85, 11.99, 14.15 μm.

<u>Nmr</u>--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.38 (singlet, 3H) CH_3; δ 6.77 (singlet, H) H_a
δ 7.94 (singlet, 2H) NH_2; δ . 57 (singlet, H) H_b.

<u>uv (Methanol)</u>--λ_{max} = 205.6 nm, A = 0.667, ε = 24,500
λ_{max} = 231.4 nm, A = 0.426, ε = 15,700
λ_{max} = 262.0 nm, A = 0.376, ε = 13,800
λ_{max} = 331.0 nm, A = 0.302, ε = 11,100.

<u>Purity</u> (99.8 ± 0.2%)

Elemental Analysis--

Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.6; H, 3.6; N, 21.3

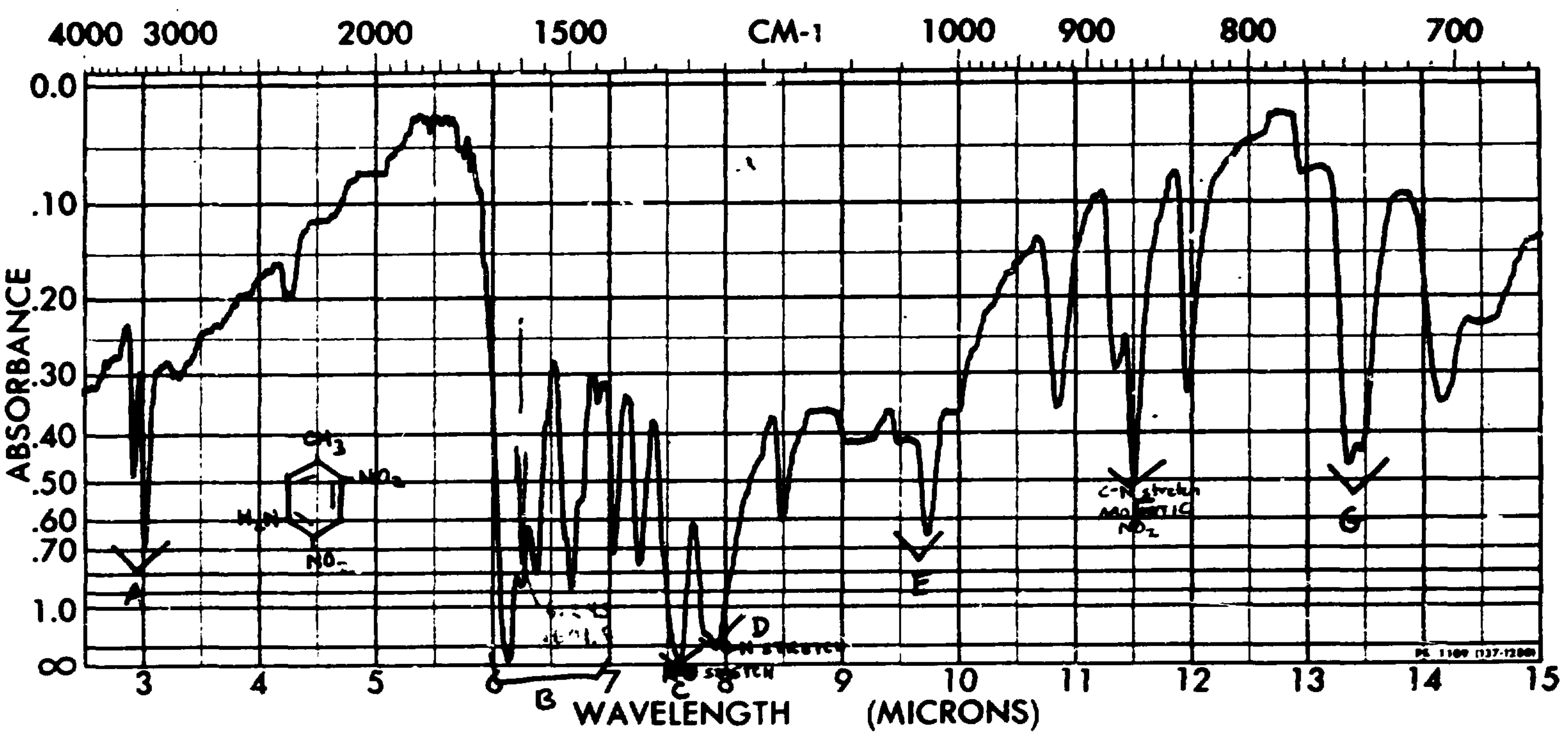
Found: C, 41.94; H, 3.51; N, 20.97.

High-Pressure Liquid Chromatography--One major component (representing 99.6% of the total peak areas) and two minor components were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Average retention time: 615 sec 5-amino-2,4-dinitrotoluene 99.6%; 52 sec impurity 0.2%; 99 sec impurity 0.2%.

Gas Chromatography--One major peak (representing 100% of the total peak areas) was observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 160 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 870 sec 5-amino-2,4-dinitrotoluene 100%.



SPECTRUM NO. 16	ORIGIN	LEGEND A: N-H stretch- 1° Aromatic Amines	REMARKS SLOW SLIT = 1
SAMPLE 5-AMINO-2,4- (KBr PELLET)	DINITROTOLUENE	1. B: C=C ring stretch; N-H bend; N=O stretch symmetric	C: N=O stretch asymmetric
	PURITY	2.	D: C-N stretch - 1° Aromatic Amines
I.D.: Recrystallized 4-15-77	PHASE	DATE MAY 6, 1977	E: In plane C-H bend F: Ar-NO₂ C-N stretch
	THICKNESS	OPERATOR C. INGERSOLL	G: Out of plane C-H bend

SPECTRUM NO. 33
SAMPLE

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK

FIGURE 122 INFRARED SPECTRUM OF 5-AMINO-2,4-DINITROTOLUENE

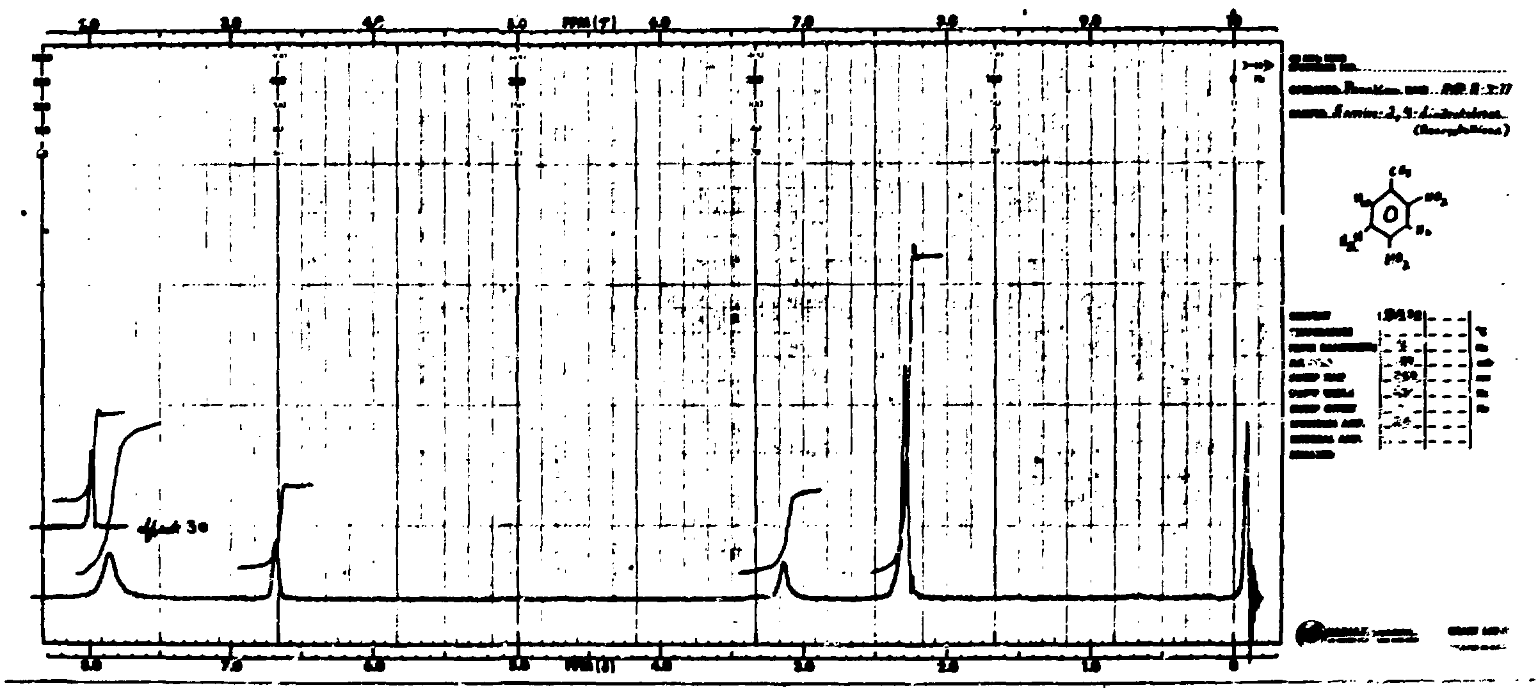


FIGURE 123 NMR SPECTRUM OF 5-AMINO-2,4-DINITROTOLUENE

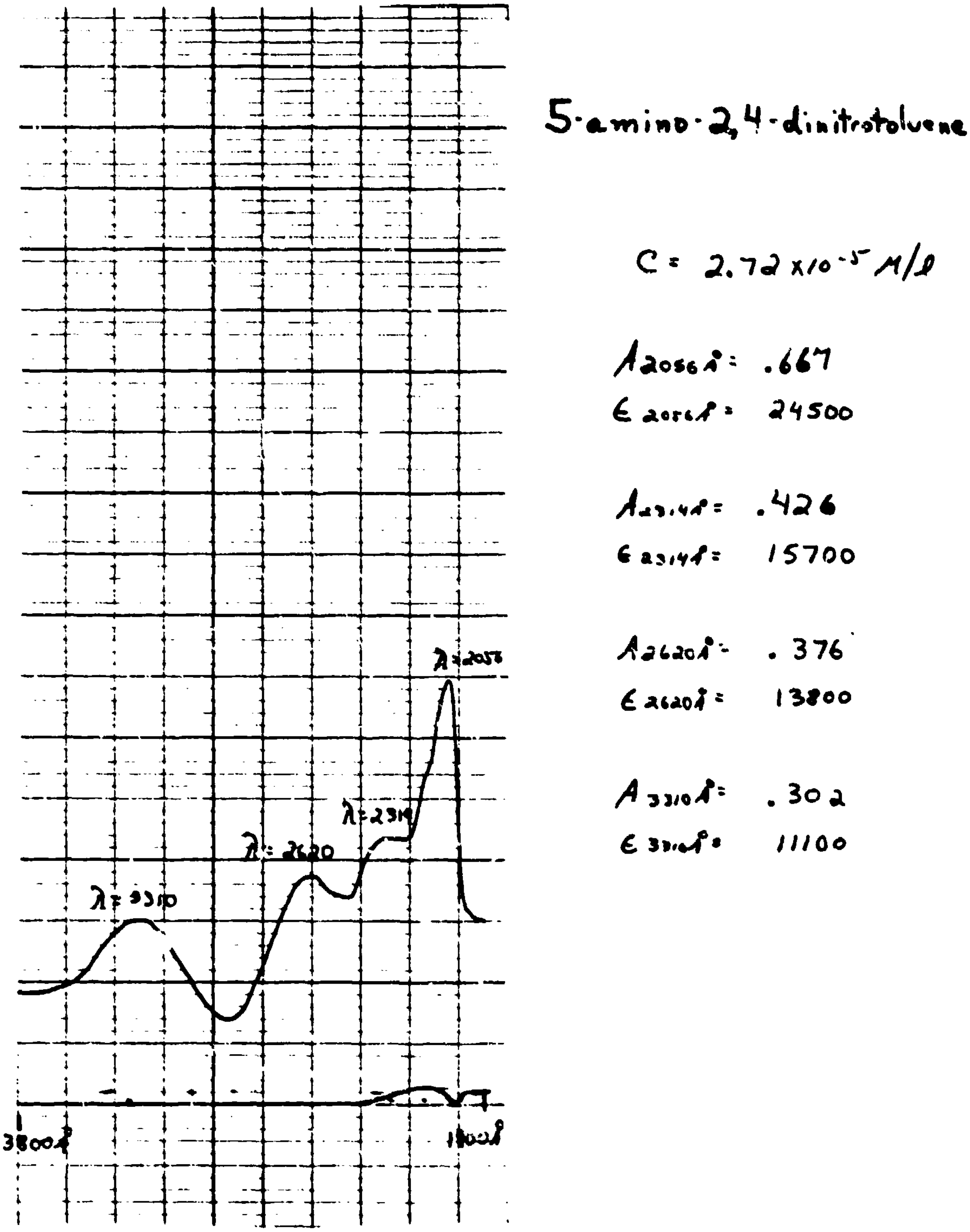


FIGURE 124 UV SPECTRUM OF 5-AMINO-2,4-DINITROTOLUENE

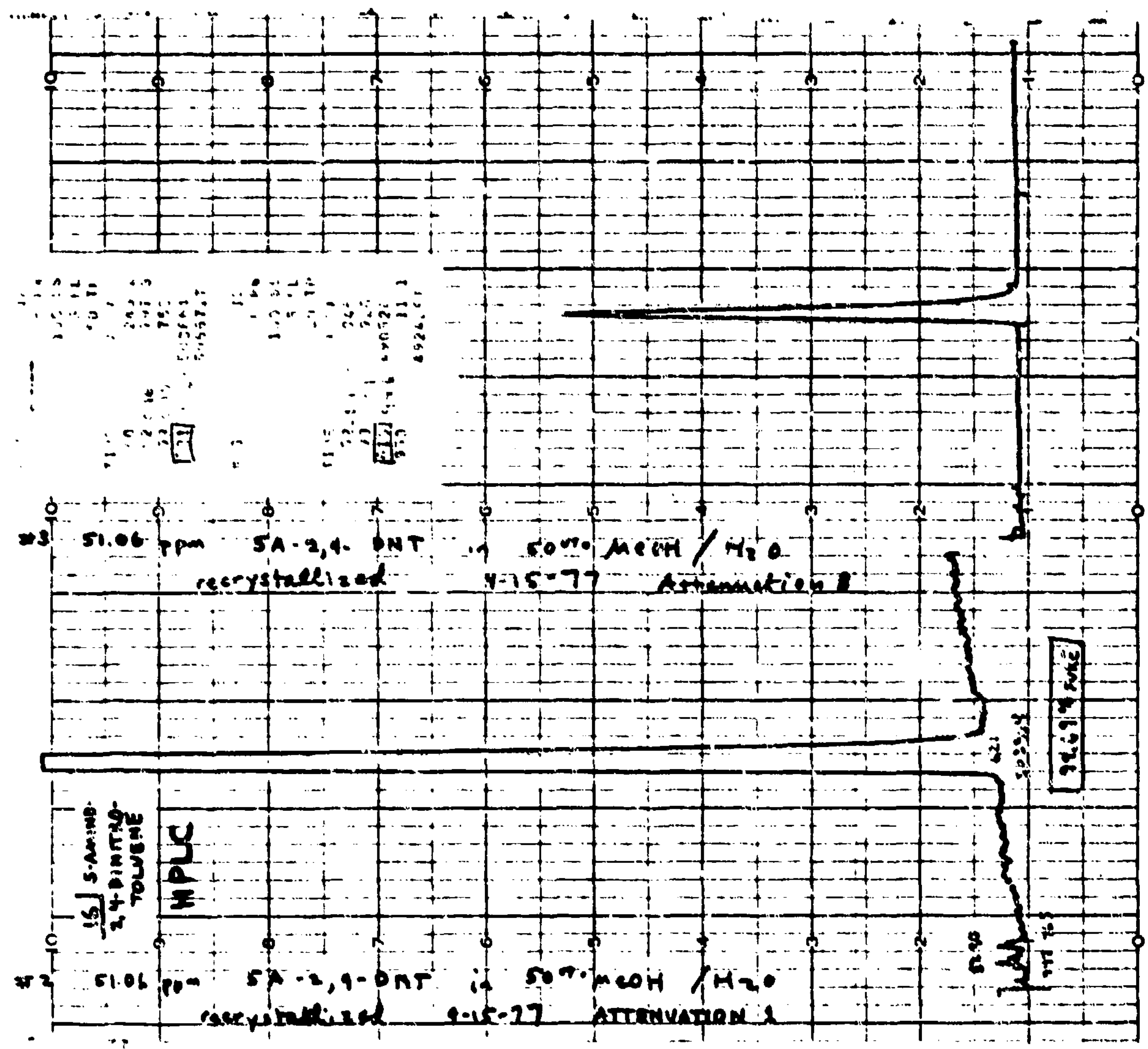


FIGURE 125 HPLC CHROMATOGRAM OF 5-AMINO-2,4-DINITROTOLUENE

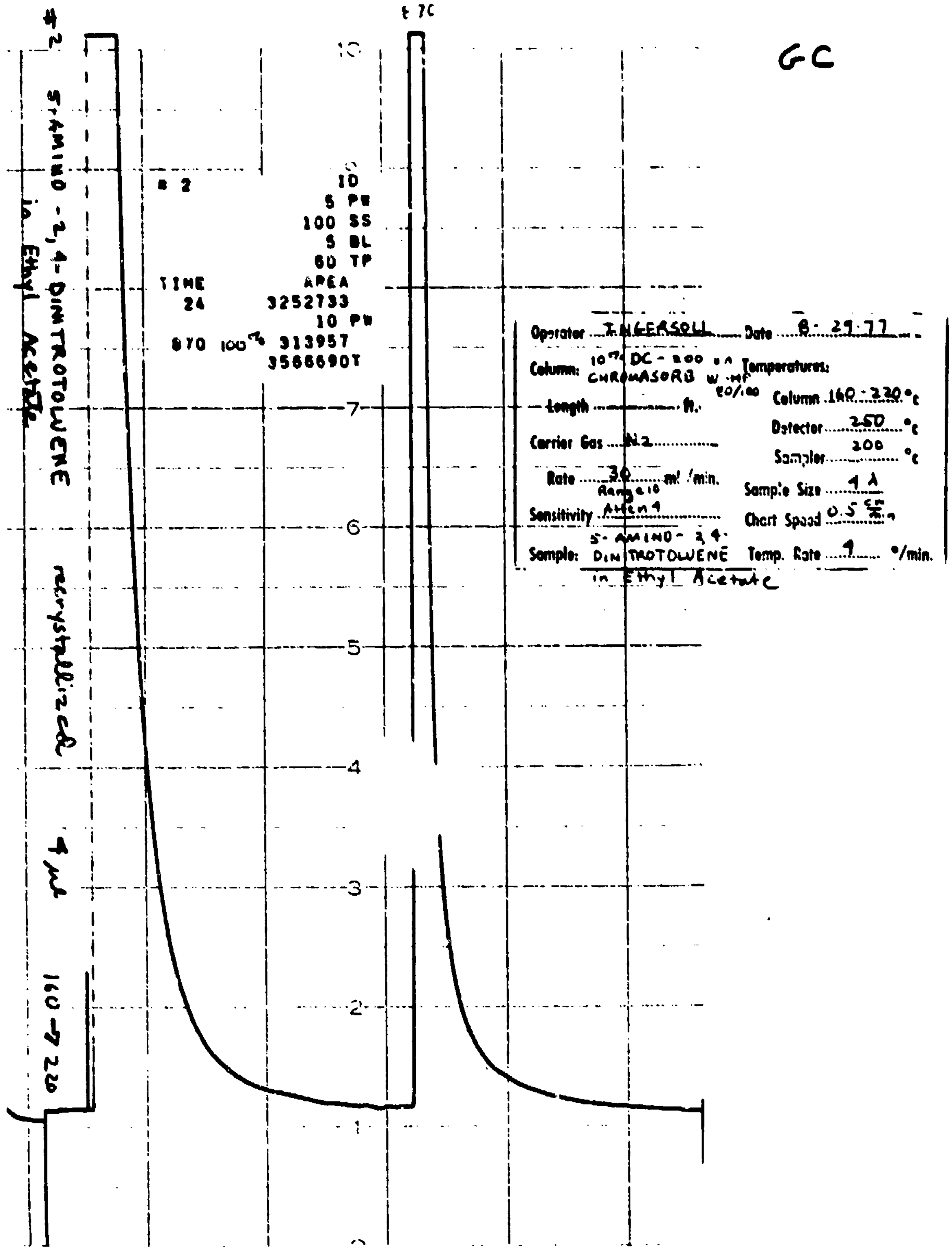


FIGURE 126 GC SPECTRUM OF 5-AMINO-2,4-DINITROTOLUENE

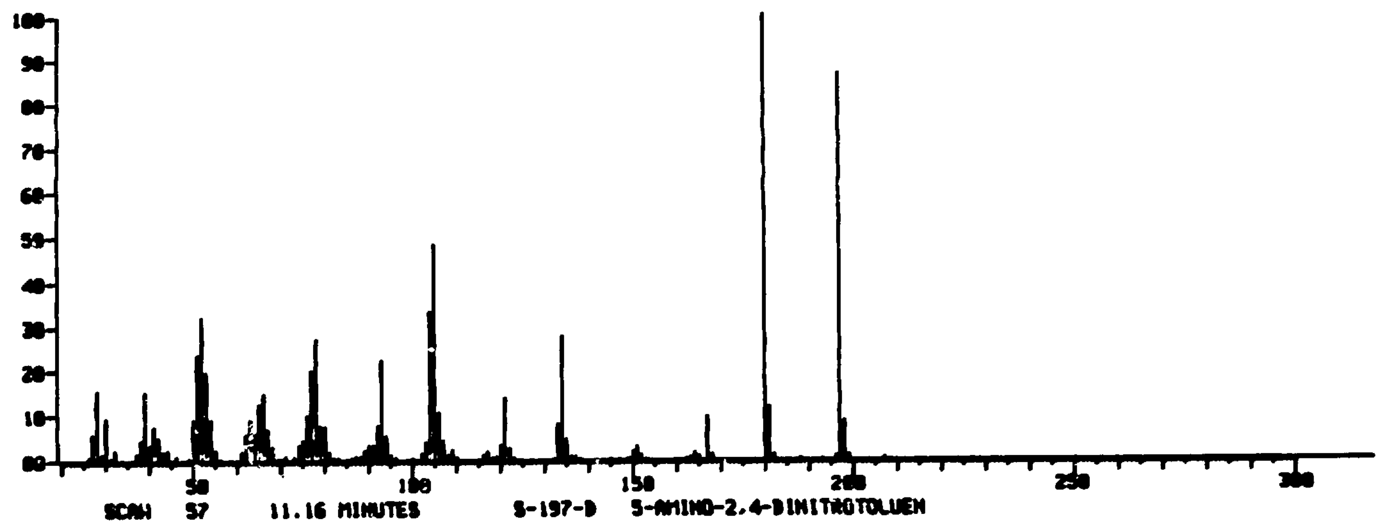
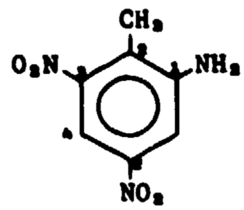


FIGURE 127 MASS SPECTRUM OF 5-AMINO-2,4-DINITROTOLUENE

4.21 2-Amino-4,6-Dinitrotoluene
2-Methyl-3,5-dinitrobenzenamine
[35572-78-2]



Source: Naval Surface Weapons Center (obtained from Aldrich Chemical Co. under Navy Contract N60921-75-C-0251, September 1975)

Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 2.9, 3.0 (N-H, 1° aromatic amines), 6.1 (C=C, ring), 6.5, 7.4 (N=O), 9.5 (C-H), 11.3 (C-N, aromatic NO_2), 13.55 (C-H and/or N-H), 10.4, 10.75, 12.3, 12.8, 14.1 μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.07 (singlet, 3H) CH_3; δ 6.08 (singlet, 2H) NH_2;
δ 7.58 (singlet, 2H) H; 2.4 (DMSO) and 3.2 (H_2O).

uv (Methanol)--λ_{max} = 227.0 nm, A = 0.729, ϵ = 20,600.

Purity (99.9 ± 0.1%)

Elemental Analysis--

Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.6; H, 3.6; N, 21.3
Found: C, 42.41; H, 3.59; N, 21.25.

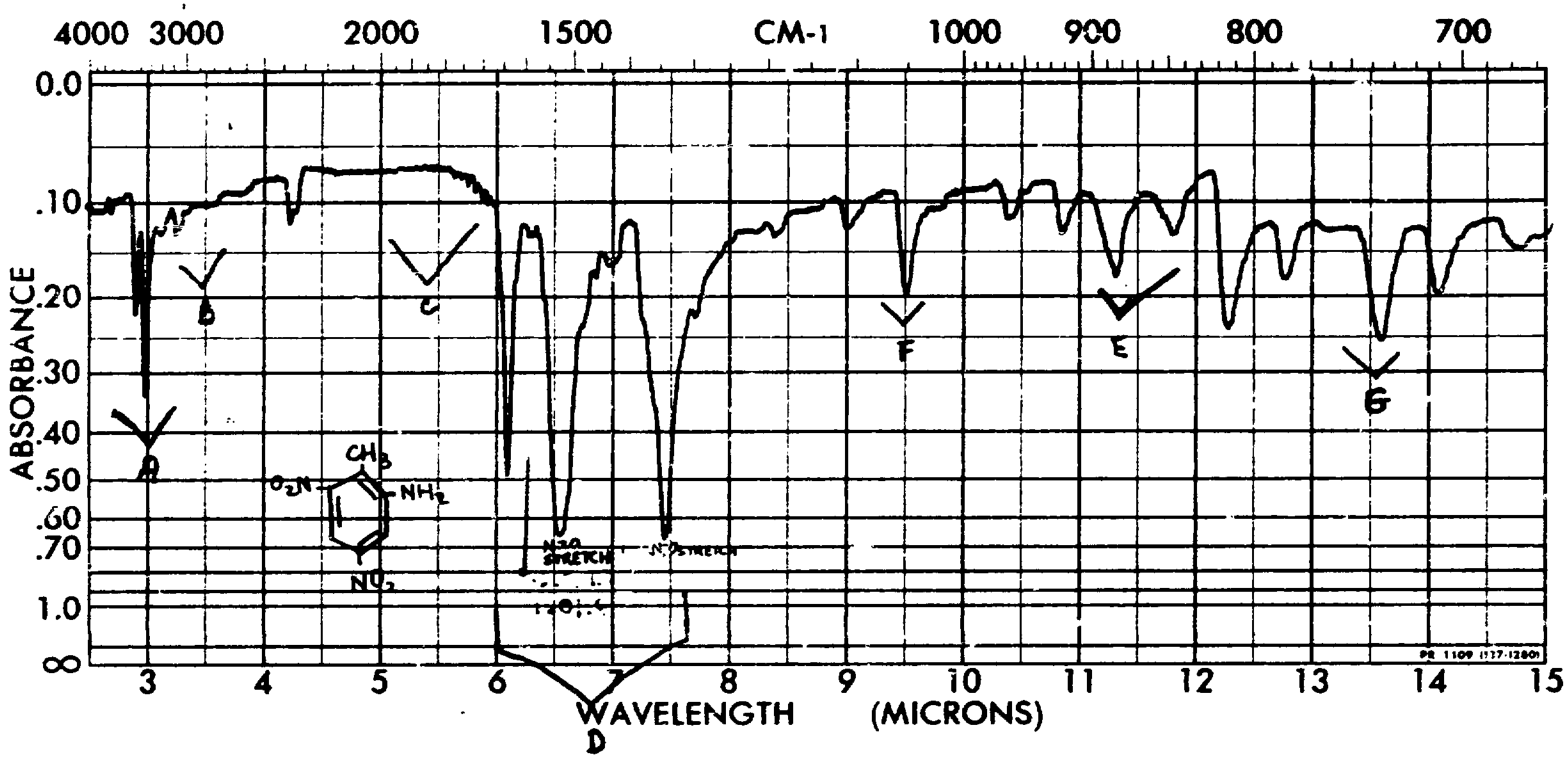
High-Pressure Liquid Chromatography--One major peak (representing 100% of the total peak areas) was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH

- Flow rate: 1.6 ml/min
- Retention time: 553 sec 2-amino-4,6-dinitrotoluene 100%.

Gas Chromatography--One major component (representing 99.8% of the total peak areas) and one minor component were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 110 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 1574 sec 2-amino-4,6-dinitrotoluene 99.8%; 1124 sec impurity 0.2%.



SPECTRUM NO. 15	ORIGIN	LEGEND	REMARKS SLOW SLIT = 1
SAMPLE 2-AMINO-4,6-DINITROTOLUENE (KBr PELLET)		1. F: In plane C-H bend G: Out of plane C-H bend or N-H wag	A: N-H B: No aromatic C-H C: No overtones; can't tell type of substitution. D: C=C ring stretch; N-H; C-N; $ArNO_2$ N=O assymetric 6.5 μ
	PURITY	2.	$ArNO_2$ N=O symmetric 7.4 μ
I.D.: LOT SR1 # 4	PHASE	DATE MAY 6, 1977	E: $ArNO_2$ C-N
	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO. 32
SAMPLE

RECORDING CHARTS

FIGURE 128 INFRARED SPECTRUM OF 2-AMINO-4,6-DINITROTOLUENE

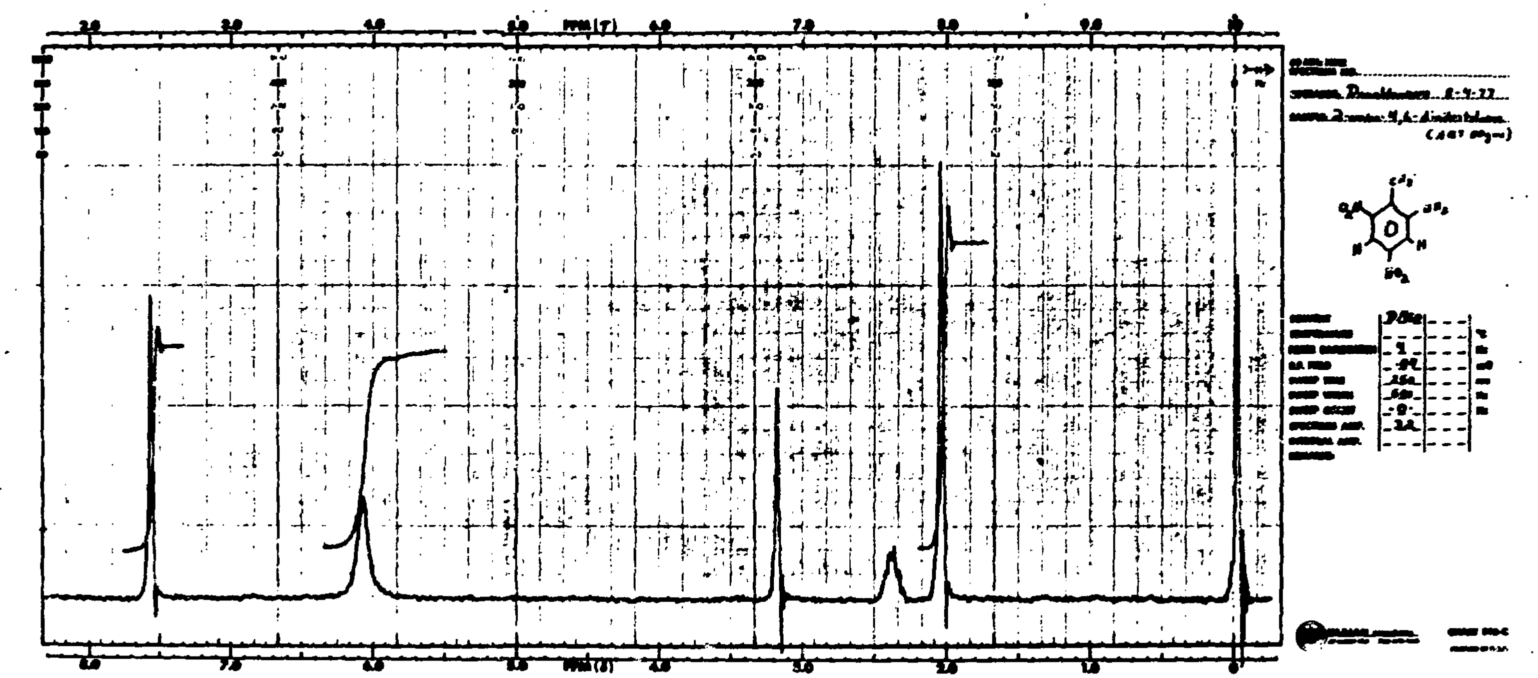


FIGURE 129 NMR SPECTRUM OF 2-AMINO-4,6-DINITROTOLUENE

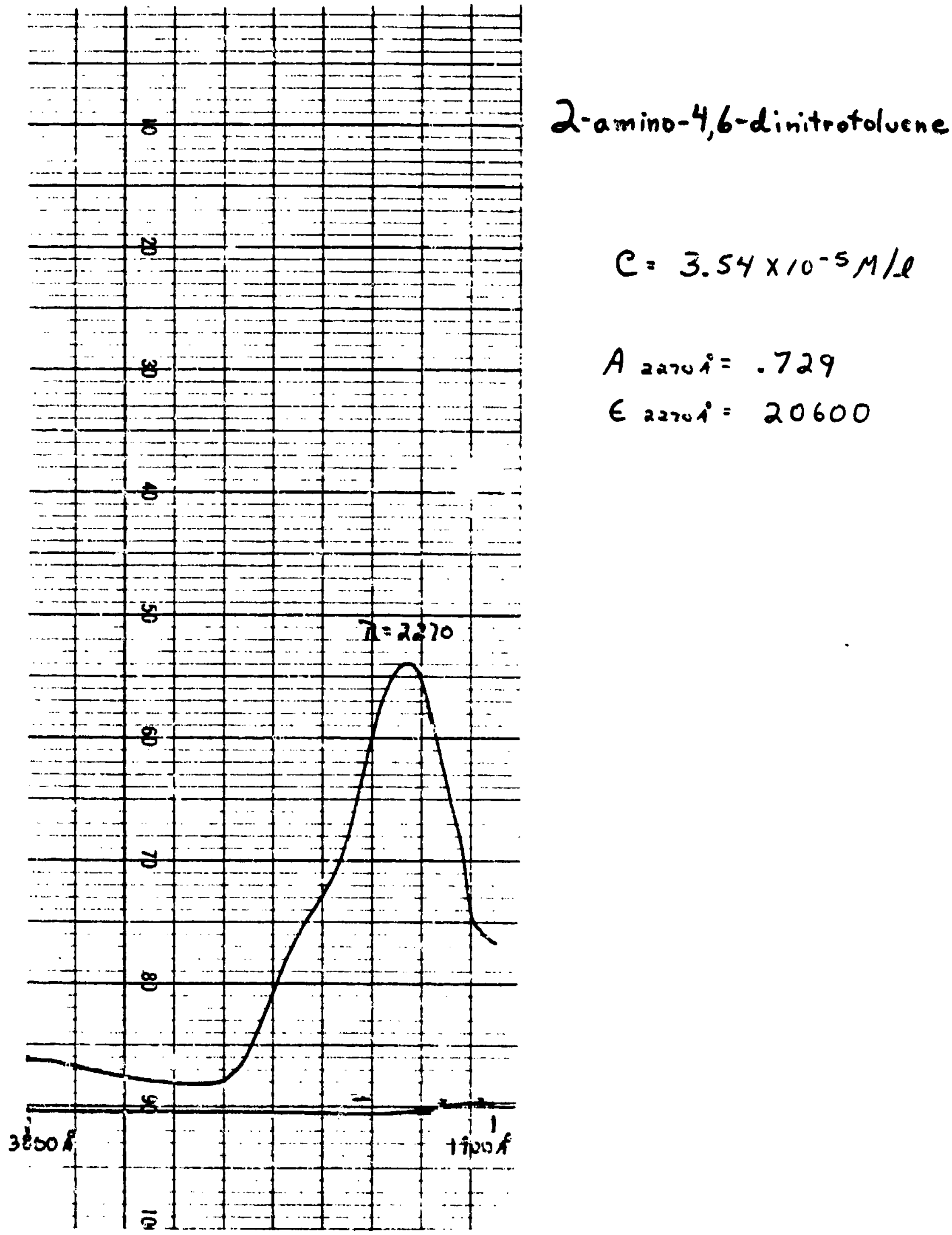


FIGURE 130 UV SPECTRUM OF 2-AMINO-4,6-DINITROTOLUENE

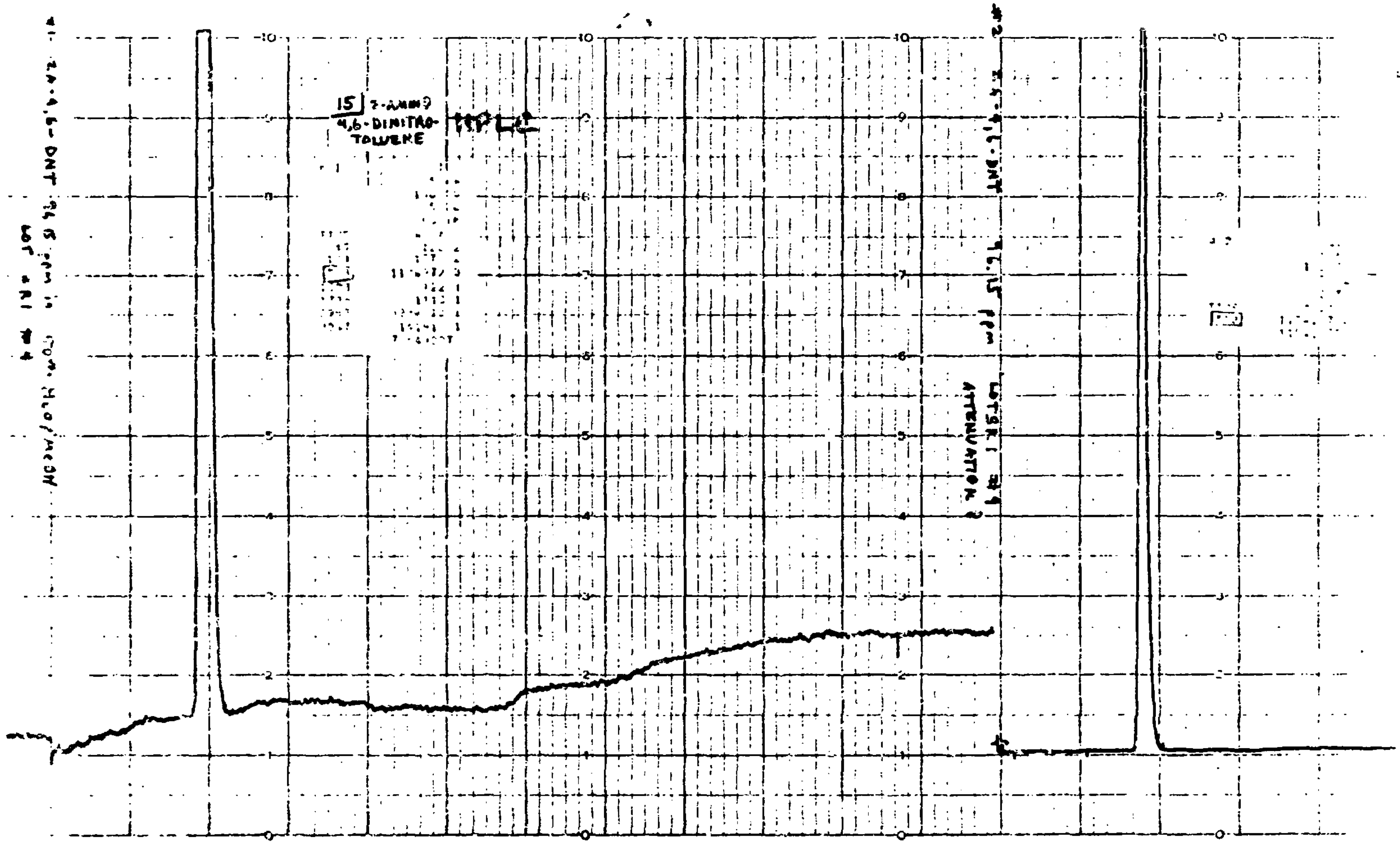


FIGURE 131 HPLC CHROMATOGRAM OF 2-AMINO-4,6-DINITROTOLUENE

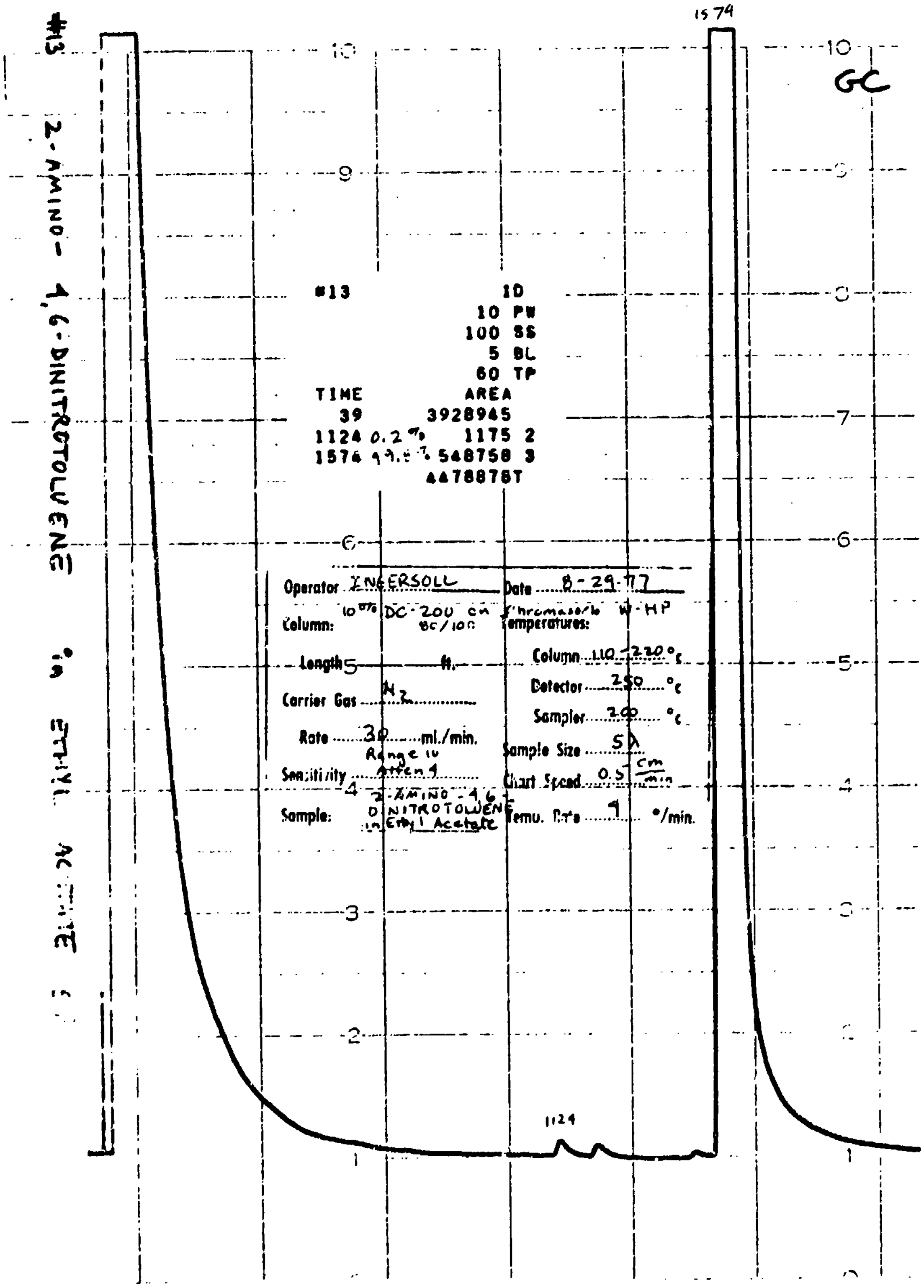


FIGURE 132 GC SPECTRUM OF 2-AMINO-4,6-DINITROTOLUENE

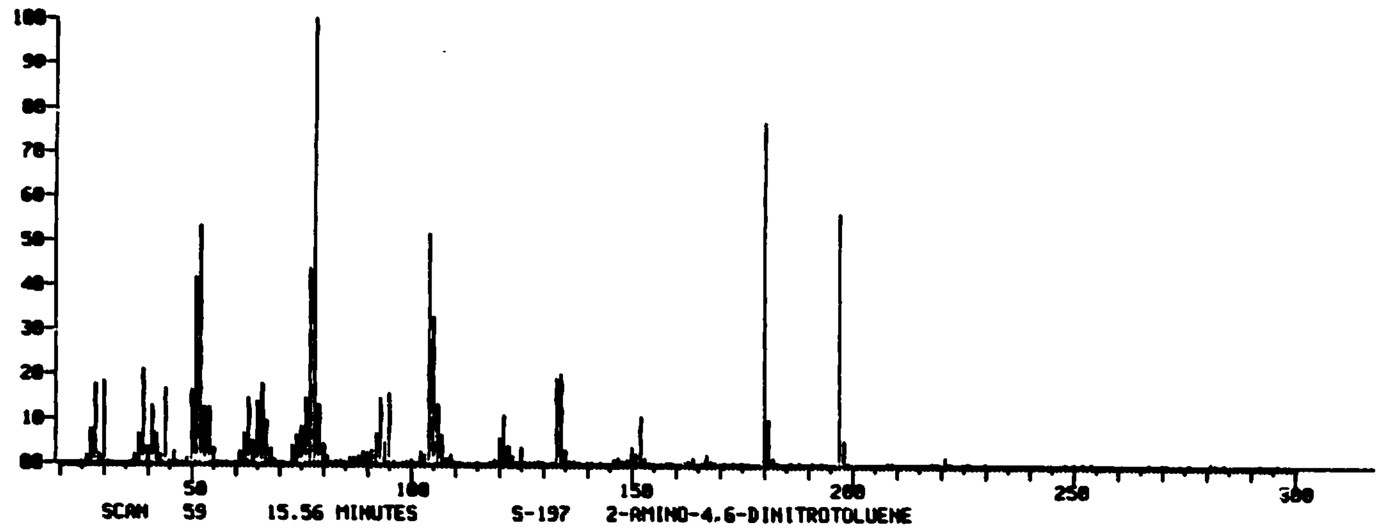
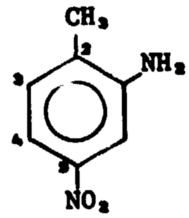


FIGURE 133 MASS SPECTRUM OF 2-AMINO-4,6-DINITROTOLUENE

4.22 <u>2-Amino-4-Nitrotoluene</u>
2-Methyl-5-nitrobenzenamine
[99-55-8]



Source: Pfaltz & Bauer
Lot number not given
Catalog No. M22730

Identity

<u>Ir</u>—The ir spectrum was consistent with the proposed Structure as well as with Sadtler Reference No. 13670 for 2-amino-4-nitrotoluene (KBr wafer). The following bands were observed: (KBr pellet) 2.9, 3.0 (N-H, 1° aromatic amine), 6.1, 6.9 (C=C, ring), 6.6, 7.4 (N=O), 7.75 (C-N), 11.4 (C-N, aromatic NO_2), 13.55 (N-H, 1° aromatic amine and/or C-H), 8.8, 9.05, 9.7, 10.0, 10.55, 12.1, 12.2 μm.

<u>Nmr</u>--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.00 (singlet, 3H) CH_3; δ 5.28 (singlet, 2H) NH_2
δ 6.83 (doublet, H, J = 4 cps) H_a
δ 7.03 (doublet, H, J = 4 cps) H_b
δ 7.32 (singlet, H) H_c.

<u>uv (Methanol)</u>--λ_{max} = 203.5 nm, A = 0.795, ε = 7790
λ_{max} = 229.0 nm, A = 1.242, ε = 12,[illegible]00
λ_{max} = 251.2 nm, A = 1.215, ε = 11,900
λ_{max} = 287.0 nm, A = 0.449, ε = 4400
λ_{max} = 369.0 nm, A = 0.189, ε = 1850.

<u>Purity</u> ([illegible] 75 ± 1.65%)

Elemental Analysis--

Anal. for $C_7H_8N_2O_2$: Calcd: C, 55.3; H, 5.3; N, 18.4
Found: C, 53.18; H, 5.21; N, 18.45.

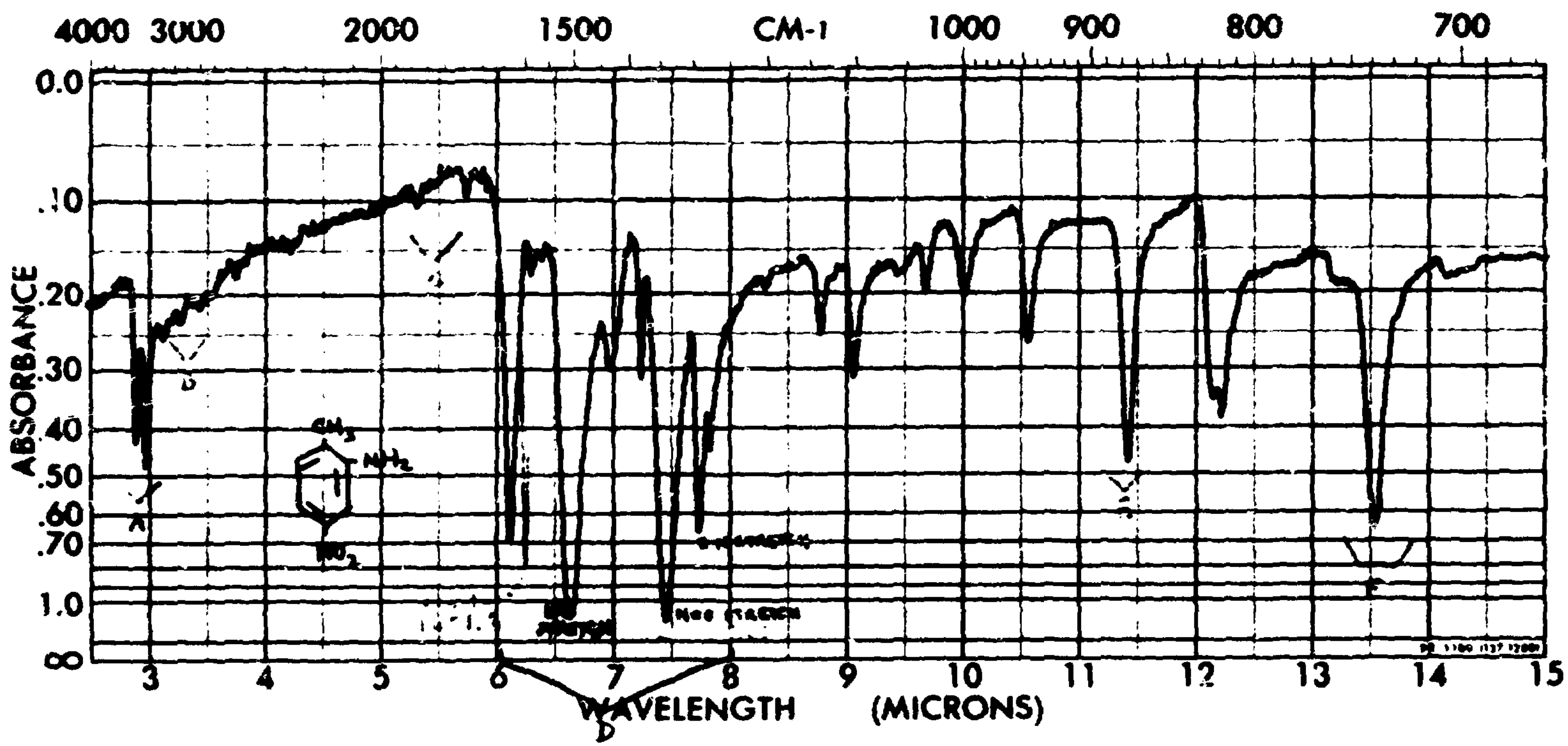
Some residue was noted.

High-Pressure Liquid Chromatography--One major component (representing 98.3 to 99.4% of the total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID × 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 60% H_2O/40% CH_3OH and 55% H_2O/45% CH_3OH
- Flow rate: 1.6 ml/min
- Detection: uv at 254 nm
- Retention time: At 60% H_2O/40% H_2O, 656 sec 2-amino-4-nitrotoluene 99.4%, 530 sec impurity 0.6%; at 55% H_2O/45% μaOH, 418 sec 2-amino-4-nitrotoluene 98.3%, 354 sec impurity 1.7%.

Gas Chromatography--One major component (representing 96.1% of the total areas) and two minor components were observed by gc under the following conditions:

- Column: 5' × 4 mm glass column packed with 10% DC-200 on Chromasorb W-HP 80/100.
- Temperature: 110 to 220°C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 995 sec 2-amino-4-nitrotoluene 96.1%; 827 sec impurity 3.3%; 1102 sec impurity 0.6%.



SPECTRUM NO. 17	ORIGIN	LEGEND A: Amine N-H stretch (1° amine) 1. B: No aromatic C-H C: Not enough resolution to det. substitution. 2.	REMARKS SLOW SLIT : 1 D: C=C ring stretch; N-H; C-N 1° Aromatic Amine stretch 6.5 μm → Ar NO₂ N=O asymmetric stretch 7.4 μm → Ar NO₂ N=O symmetric str. E: Ar NO₂ C-N stretch F: 1° Ar NH₂; Out of plane C-H bend
SAMPLE 2-AMINO-4-NITROTOLUENE (KBr PELLET)	PURITY		
I.D.: Pfaltz & Bauer, Inc. M 22730	PHASE	DATE MAY 9, 1977	
	THICKNESS	OPERATOR C. INGERSOLL	

SPECTRUM NO. 39
SAMPLE

FIGURE 134 INFRARED SPECTRUM OF 2-AMINO-4-NITROTOLUENE (KBr PELLET)

17 2-AMINO-4-NITROTOLUENE

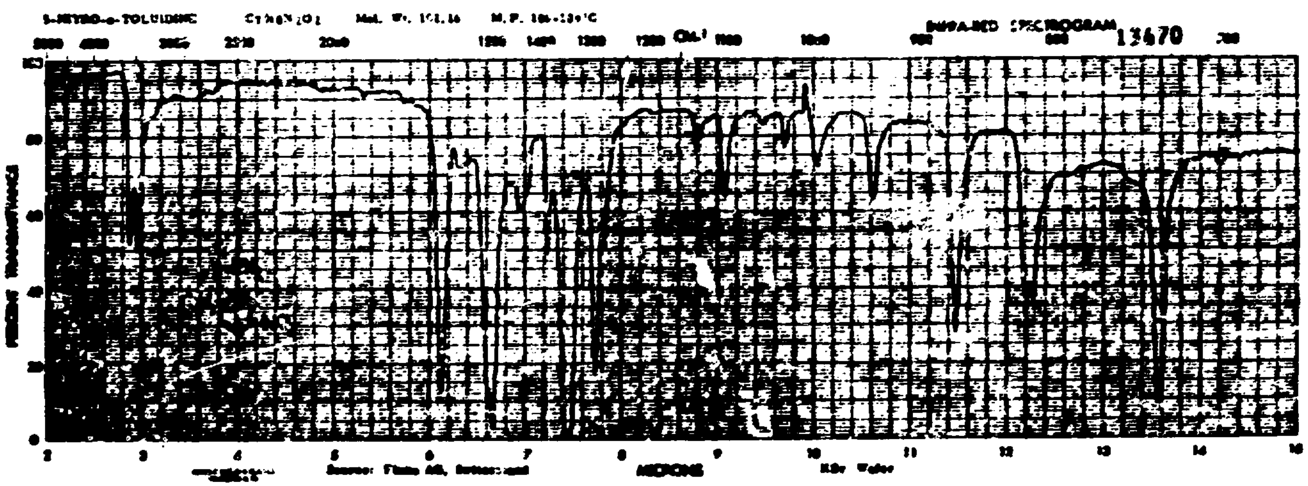


FIGURE 135 INFRARED SPECTRUM OF 2-AMINO-4-NITROTOLUENE (KBr WAFER)

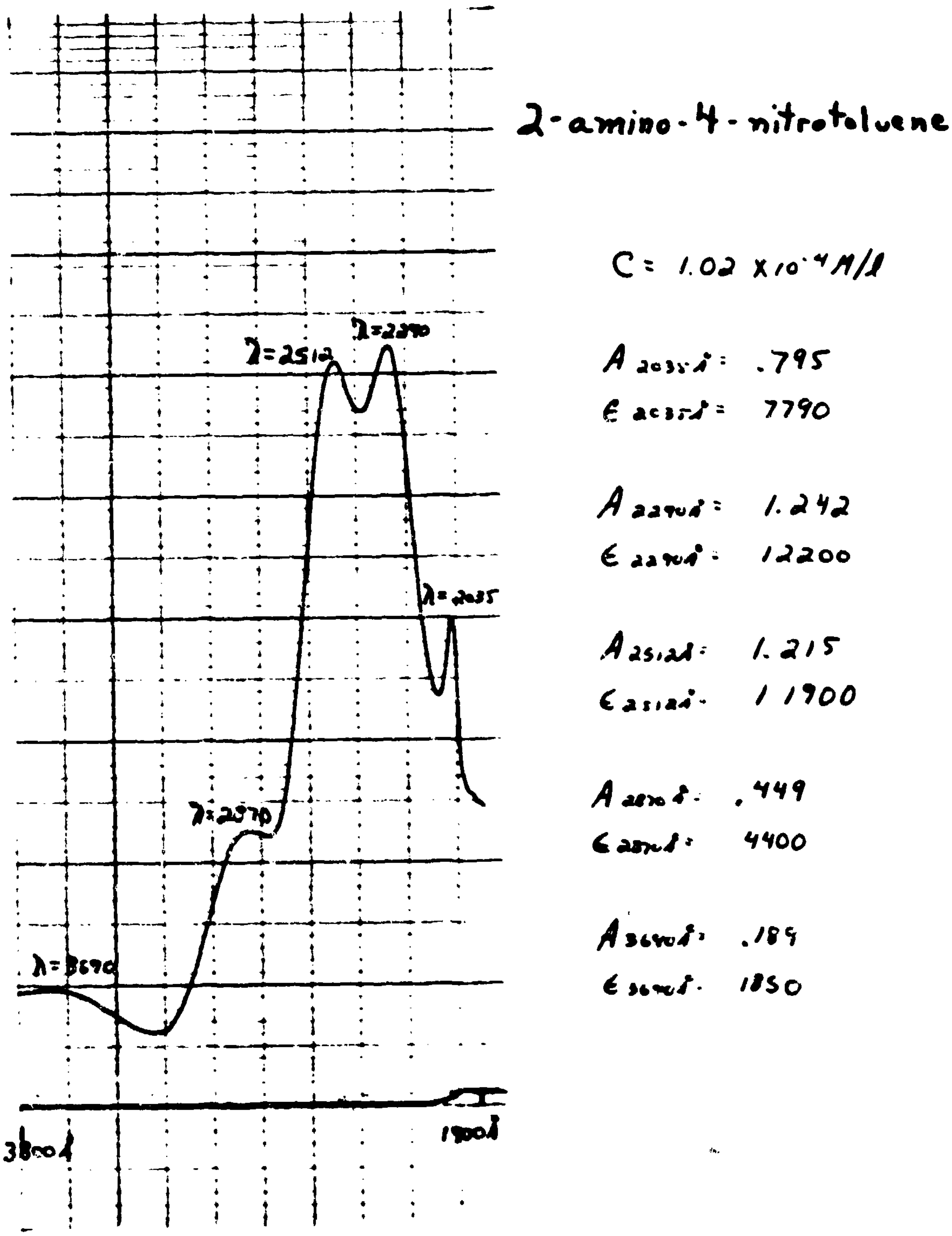


FIGURE 136 UV SPECTRUM OF 2-AMINO-4-NITROTOLUENE

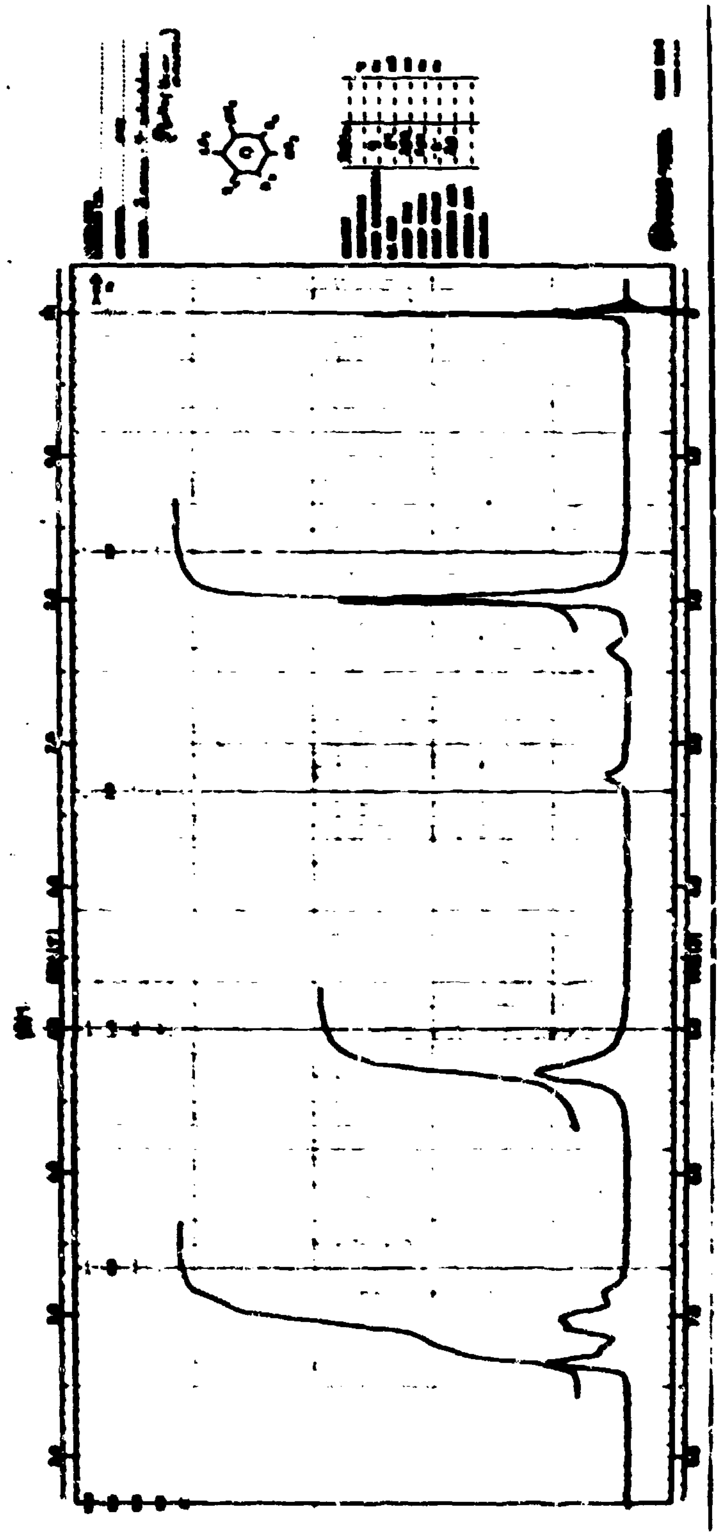


FIGURE 137 NMR SPECTRUM OF 2-AMINO-4-NITROTOLUENE

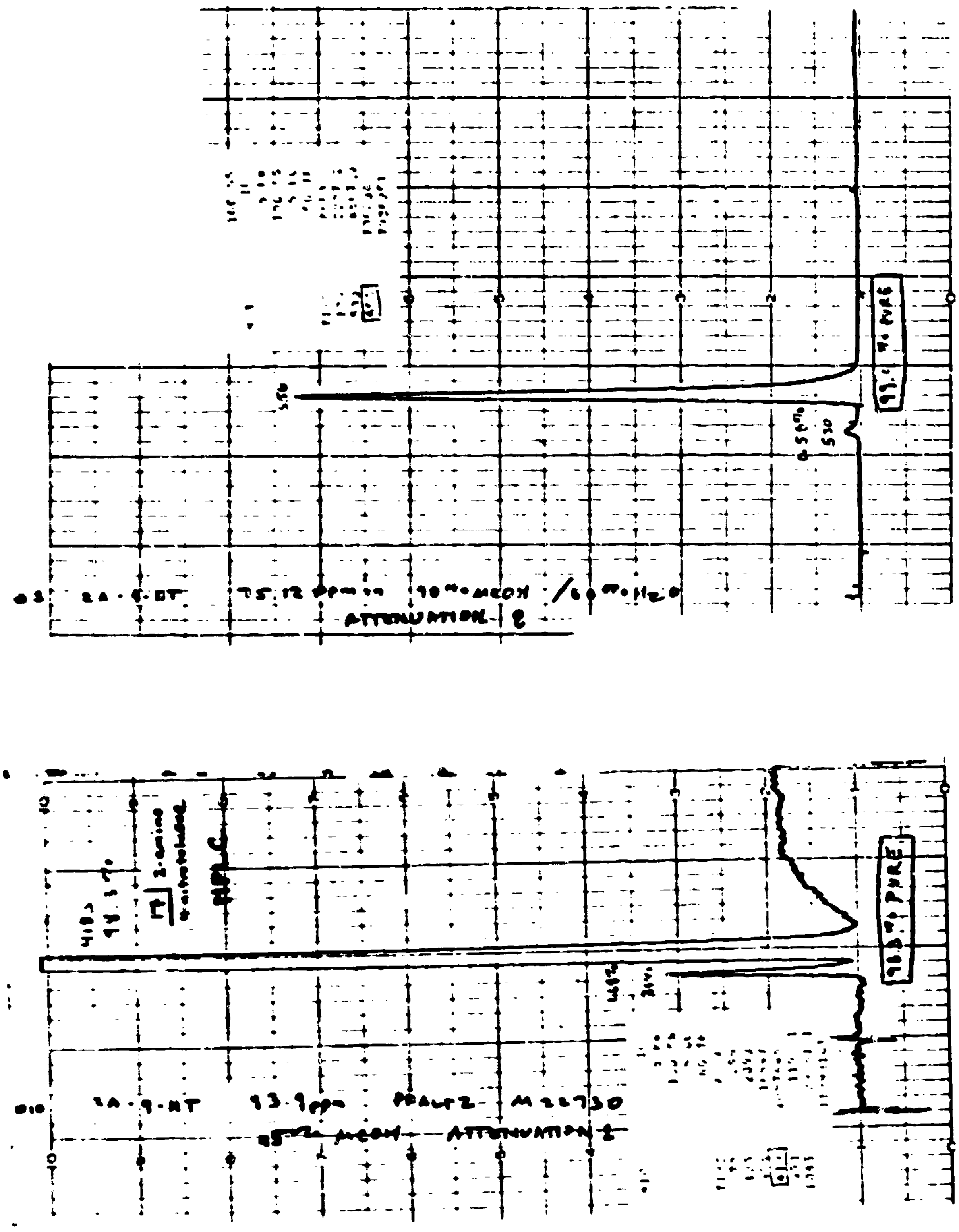


FIGURE 138 HPLC CHROMATOGRAM OF 2-AMINO-4-NITROTOLUENE

GC

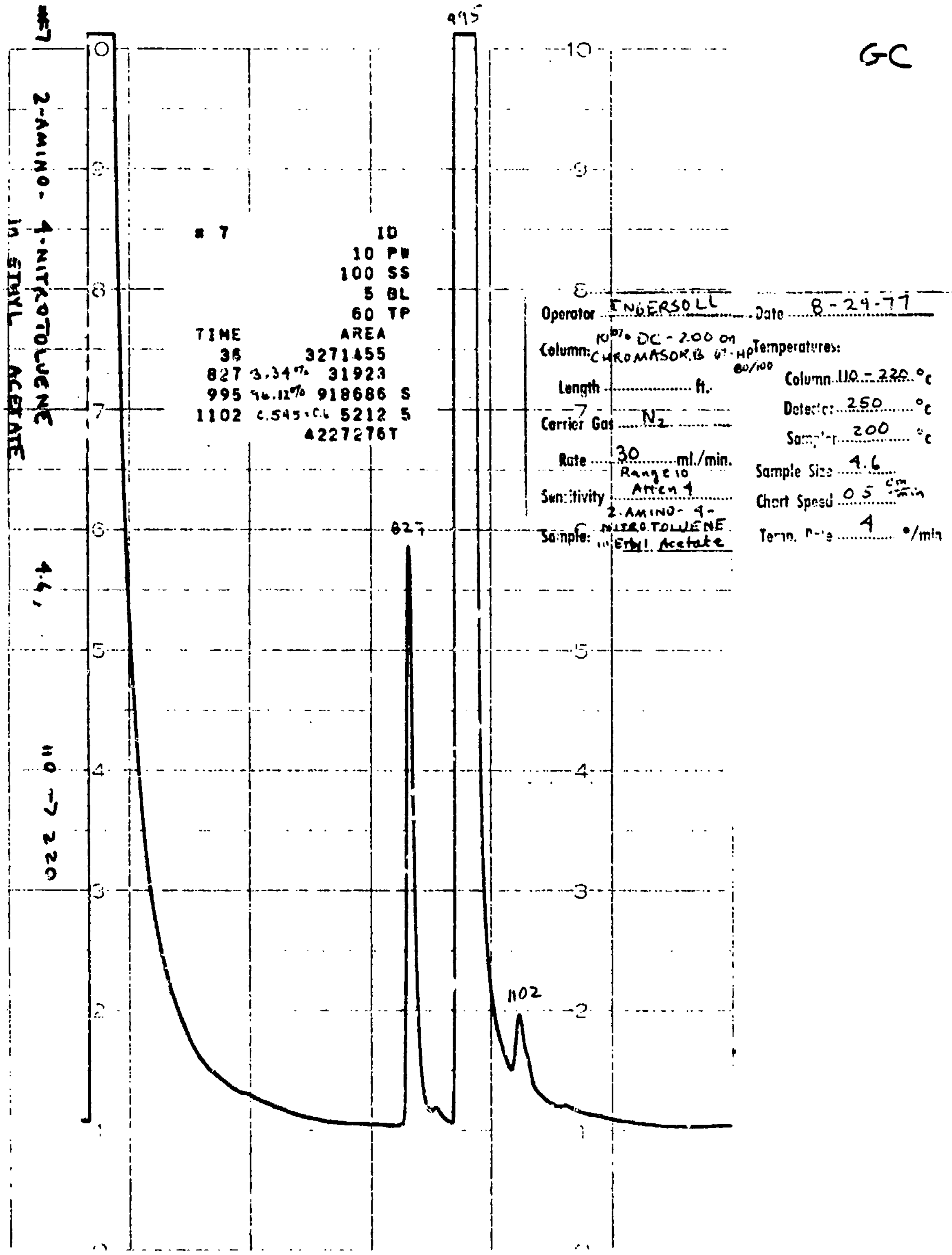


FIGURE 139 GC SPECTRUM OF 2-AMINO-4-NITROTOLUENE

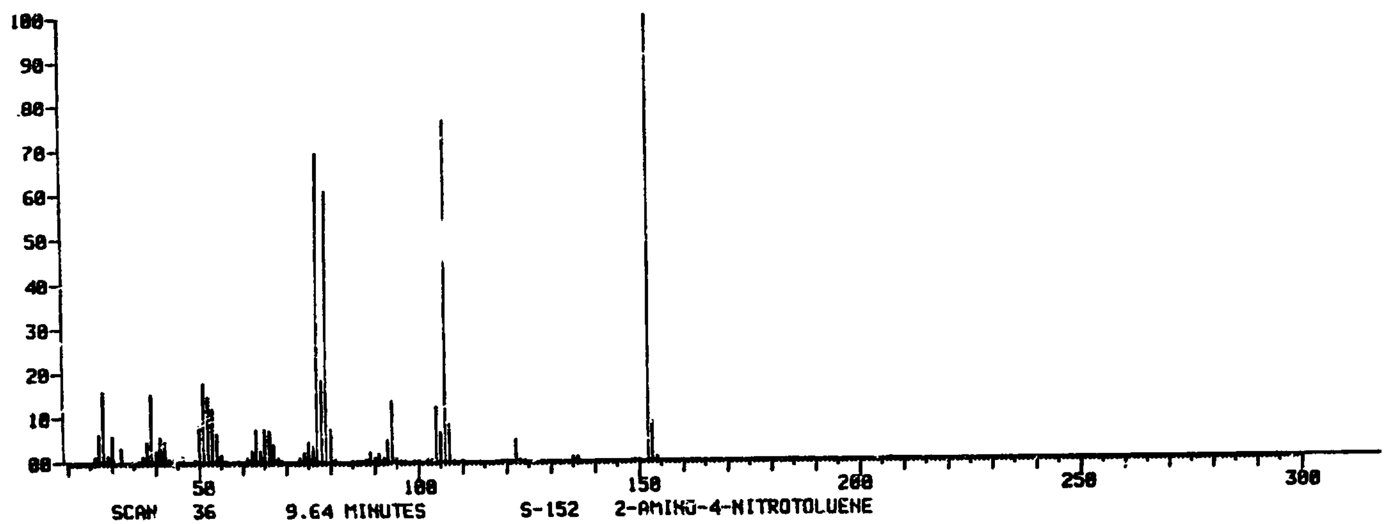
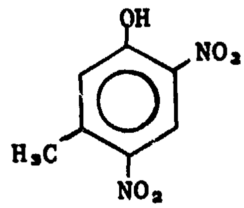
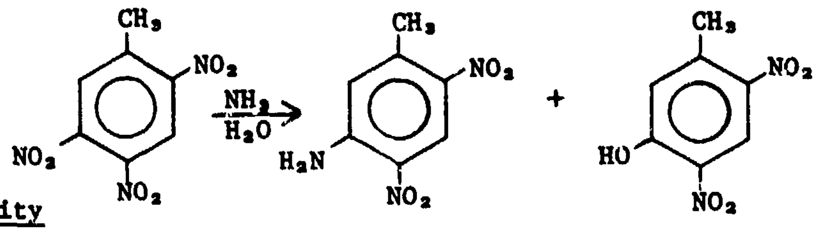


FIGURE 140 MASS SPECTRUM OF 2-AMINO-4-NITROTOLUENE

4.23 2,4-Dinitro-5-Methylphenol



Source: Synthesis, SRI



Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 3.2 (C-H, aromatic), 6.15, 6.65 (C=C, ring), 6.32, 7.69 (N=O), 8.38 (C-C), 9.7, 13.39 (C-N), 11.5, 11.95 (C-N, aromatic NO_2), 7.0, 7.85, 8.5, 9.0, 10.78, 12.9, 14.28.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.70 (singlet, 3H) CH_3
δ 7.10 (singlet, H) H_a
δ 8.90 (singlet, H) H_b
δ 10.85 (singlet, H) OH.

Uv (Methanol)--λ_{max} = 214.2 nm, A = 0.712, ε = 11,780
λ_{max} = 263 nm, A = 0.794, ε = 13,100
λ_{max} = 335.6 nm, A = 0.287, ε = 4740.

Purity (>95%)

Elemental Analysis--

Anal. for $C_7H_6N_2O_5$: Calcd: C, 42.43; H, 3.05; N, 14.14
Found: C, 42.26; H, 3.17; N, 13.86.

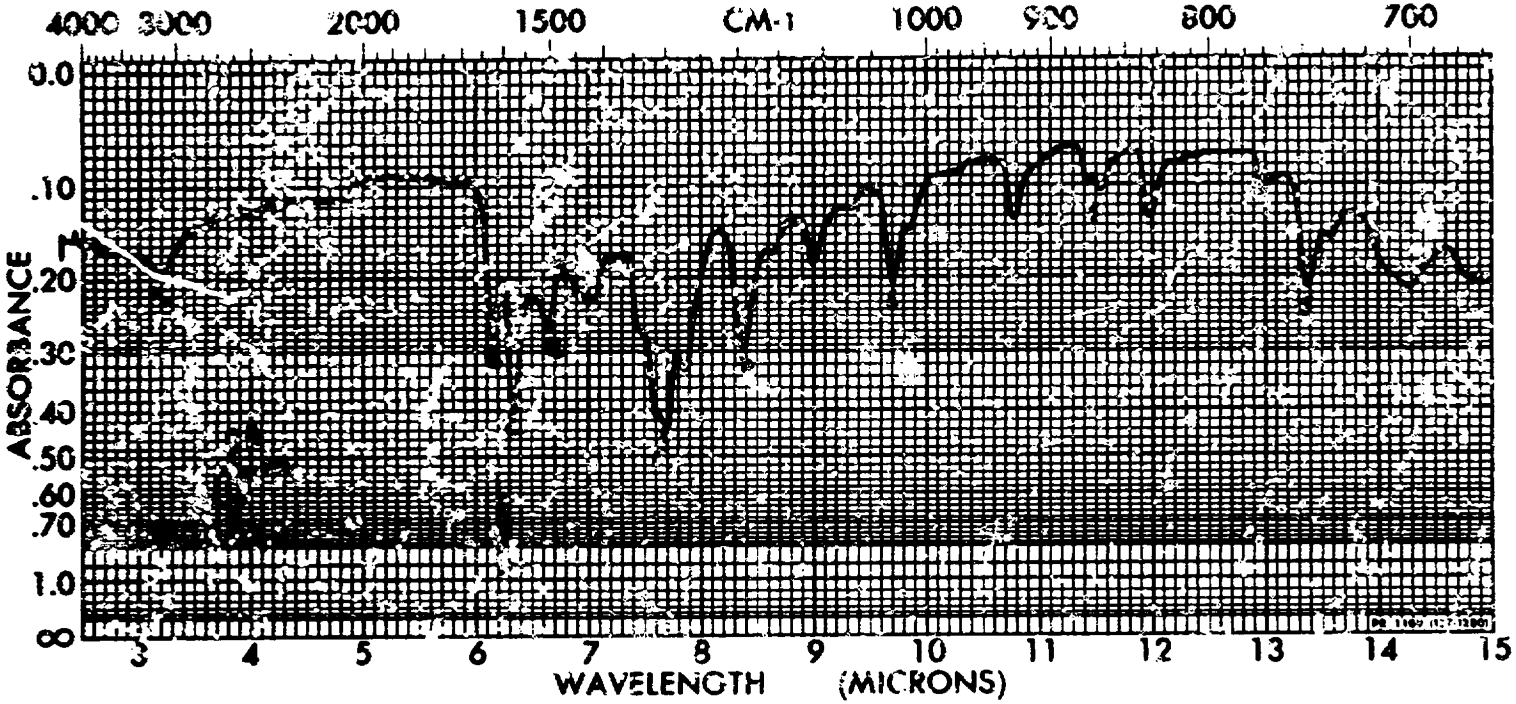
<u>High Pressure Liquid Chromatography</u>--One major component (representing 98.7% of total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 60% H_2O/40% CH_3OH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 nm

  Average retention time: 215 sec 2,4-dinitro-5-methylphenol 98.7%; 298 sec impurity 0.23%; 375 sec impurity 1.06%.

<u>Gas Chromatography</u>--One major component (representing 98.9% of total peak areas) and two minor components were observed by gc under the following conditions:

- Column: 6' x 2 mm glass column packed with 10% DC 200 on Chromasorb
- Temperature: 130° to 220° C at 4°/min
- Flow rate: 30 ml/min N_2
- Detection: Flame ionization
- Retention time: 11.62 min 2,4-dinitro-5-methylphenol 98.9%; 13.8 min impurity 0.1%; 22.2 min impurity 1.0%.

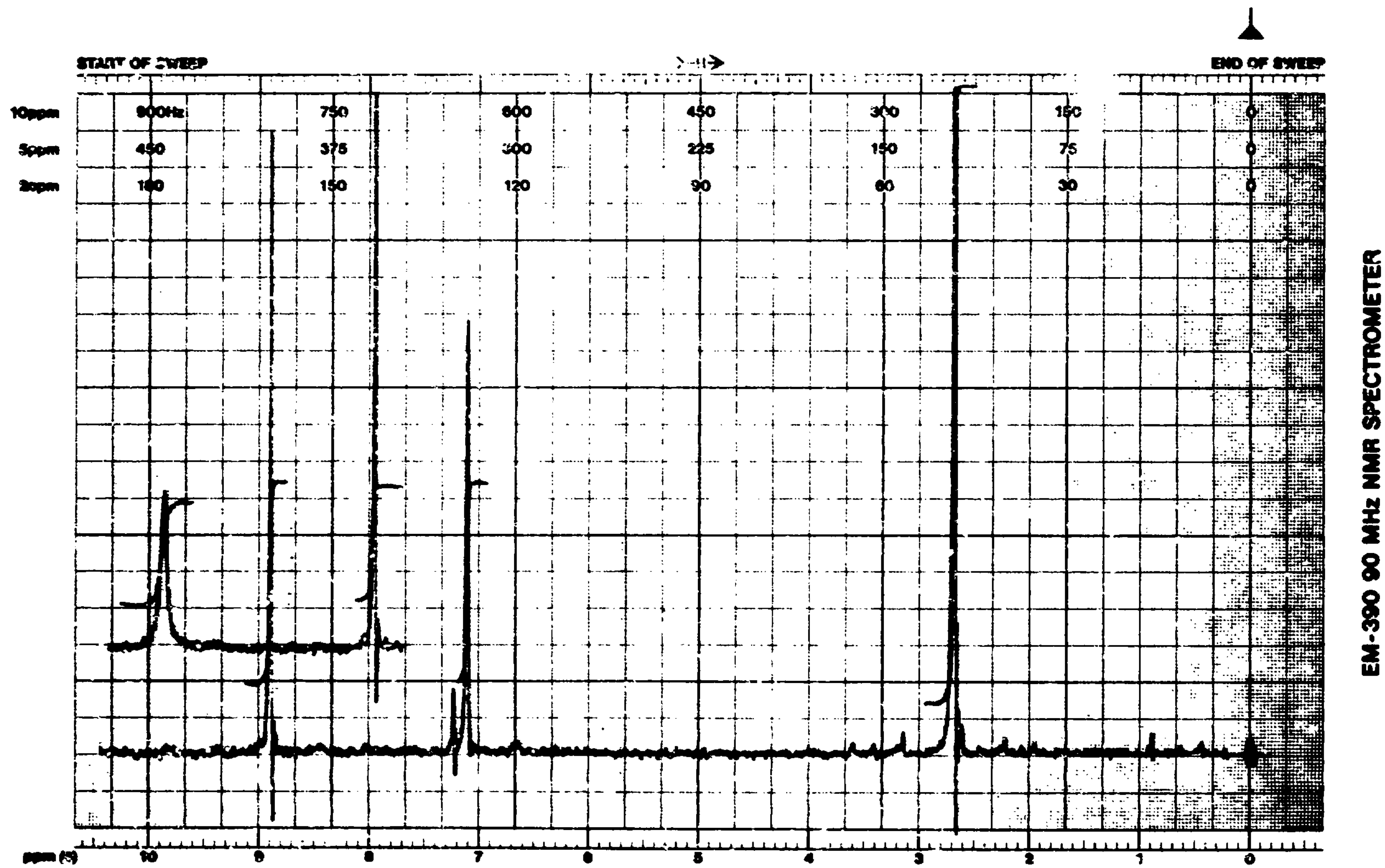


SPECTRUM NO.	ORIGIN	LEGEND ⓐ C-H, aromatic ⓑ C=C ⓒ N=O ⓓ C-H, aromatic NO_2 1. ⓔ C-O ⓕ C-H	REMARKS
SAMPLE 2,4-Dinitro-5-Methylphenol			
	PURITY	2.	
	PHASE	DATE 13 April 78	
	THICKNESS	OPERATOR Keck	

SPECTRUM NO
SAMPLE

RECORDING CHARTS

FIGURE 141 INFRARED SPECTRUM OF 2,4-DINITRO-5-METHYLPHENOL



LOCK POS. ______ ppm	SPECTRUM AMPL. 4	SWEEP TIME 5 min	NUCLEUS ______
LOCK POWER .002 mG	FILTER .05 sec	SWEEP WIDTH 10 ppm	ZERO REF. ______
DECOUPLE POS. ______ ppm	RF POWER .04 mG	END OF SWEEP ______ ppm	SAMPLE TEMP. ______ °C
DECOUPLING POWER ______ mG			

SAMPLE: 2,4-Dinitro-5-methylphenol

SOLVENT: CDCl$_3$ w/ 1% (v/v) TMS

OPERATOR KECK

DATE 4/10/78

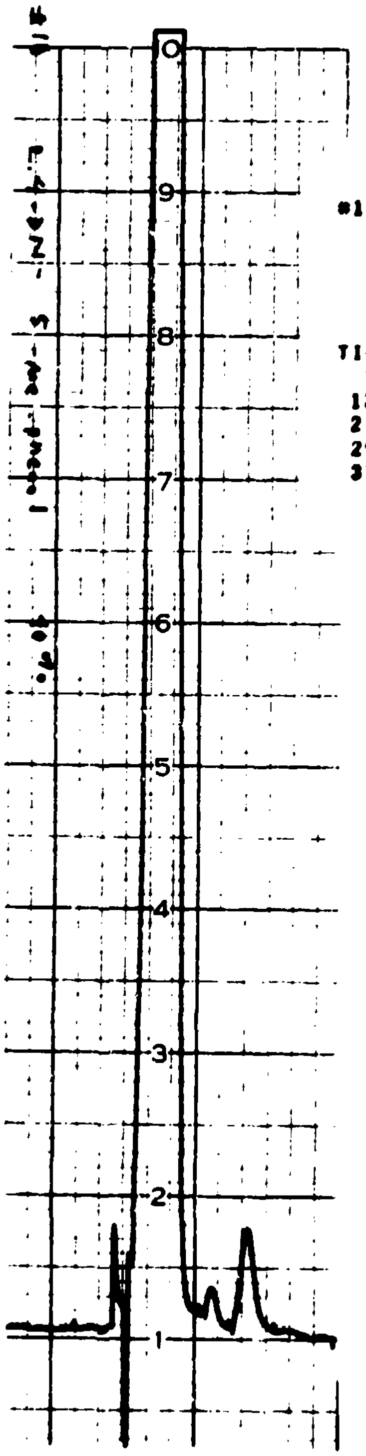
SPECTRUM NO. ______

varian instrument division palo alto, california

FIGURE 142 NMR SPECTRUM OF 2,4-DINITRO-5-METHYLPHENOL

2,4-DINITRO-5-METHYL-
PHENOL

HPLC



#18	ID		
	7 PW		
	50 SS		
	5 HL		
	60 TP		
	200 MA		
TIME	AREA		
90	8396 2		
123	5408 2		
215	903337 3	98.7%	
298	2060	0.[illegible]	
375	9693	1.06[illegible]	
	928894T		

40% CH_3OH / 60% H_2O
2.0 ml/min

MAR 29 1978

FIGURE 143 HPLC CHROMATOGRAM OF 2,4-DINITRO-5-METHYLPHENOL

026

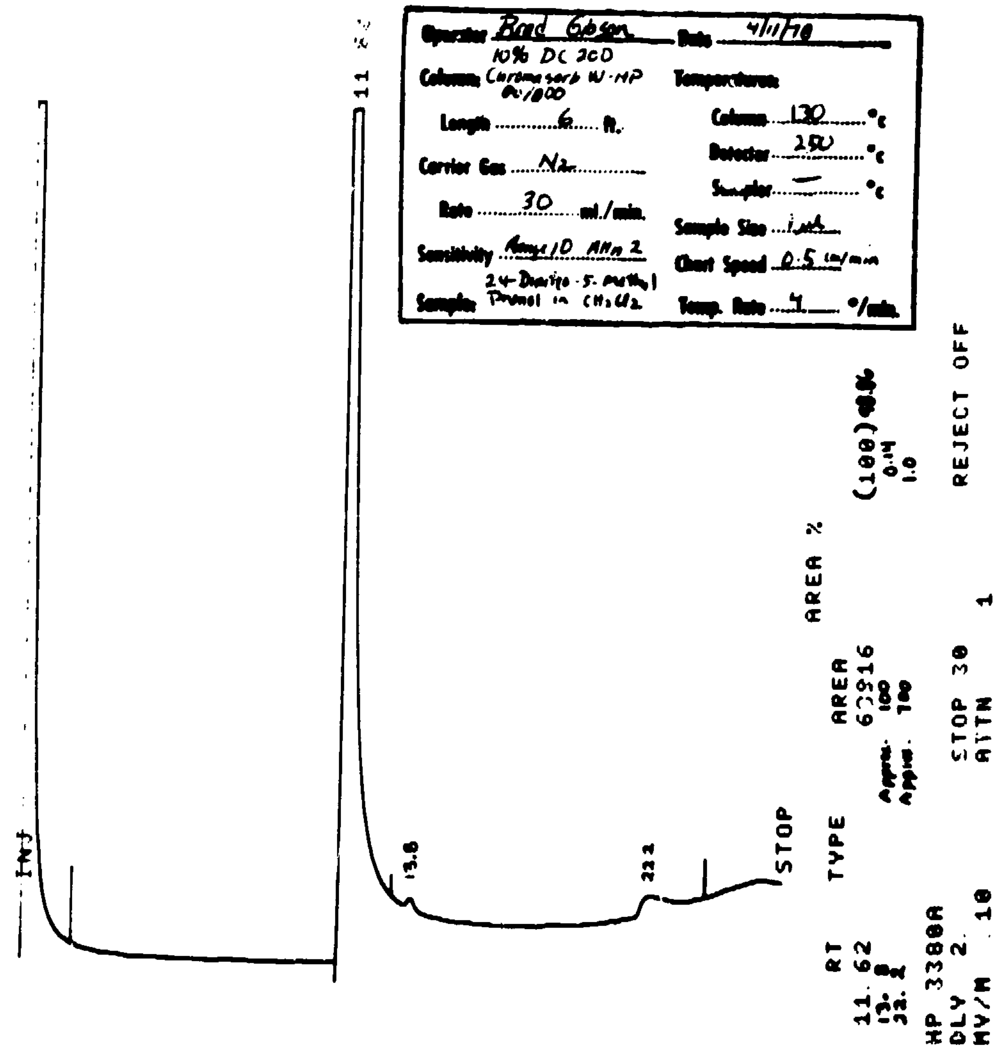


FIGURE 144 GC SPECTRUM OF 2,4-DINITRO-5-METHYLPHENOL

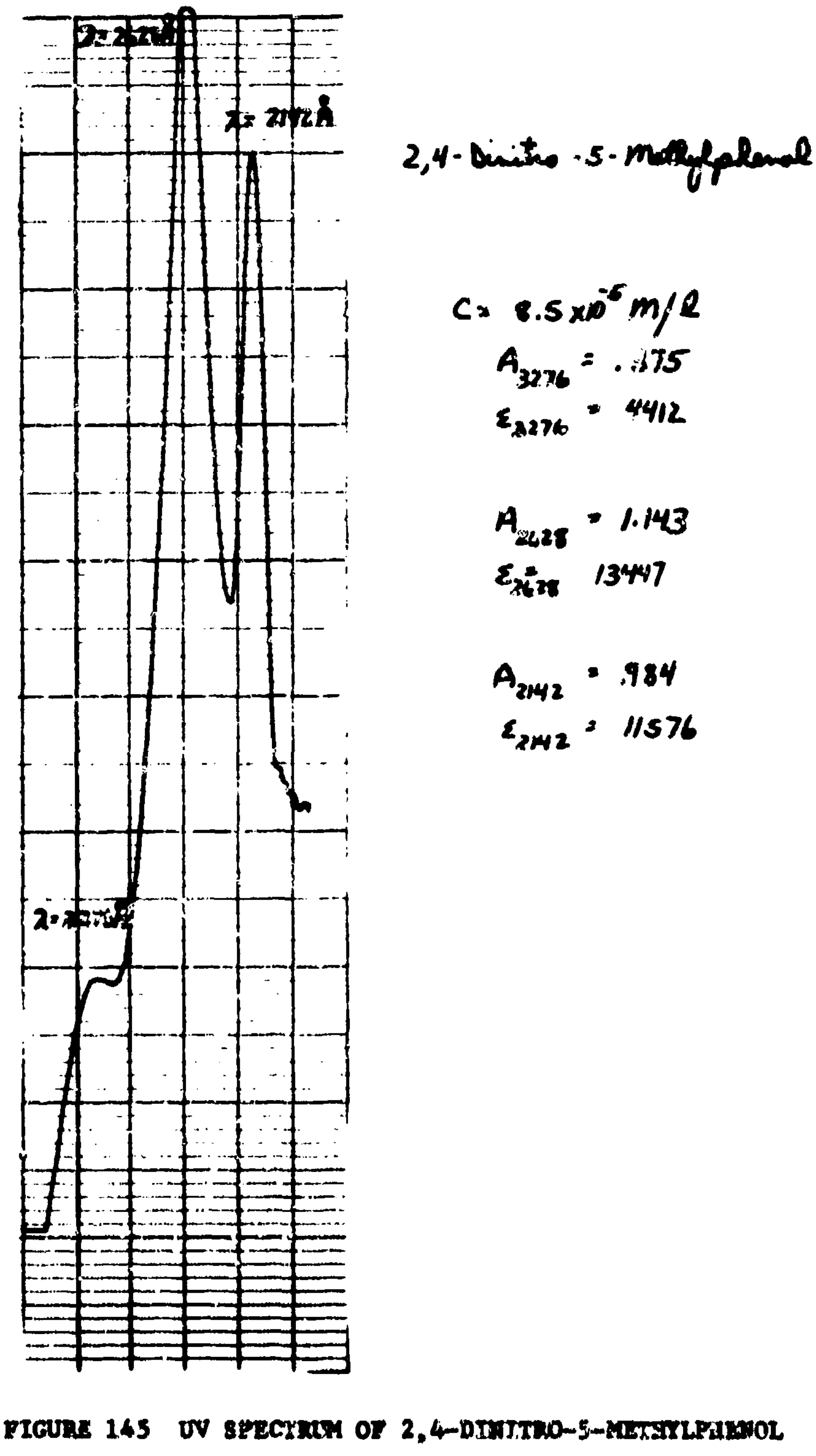


FIGURE 145 UV SPECTRUM OF 2,4-DINITRO-5-METHYLPHENOL

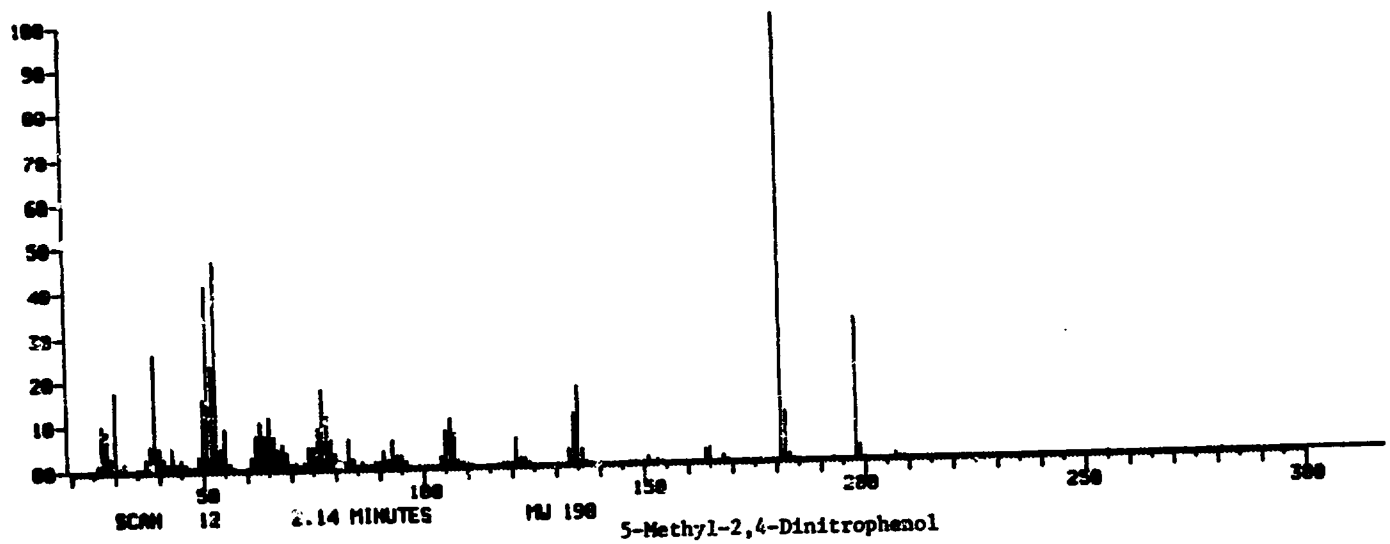


FIGURE 146 MASS SPECTRUM OF 2,4-DINITRO-5-METHYLPHENOL

4.24 4-Nitrobenzonitrile

[619-72-7]

Source: Aldrich Chemical Company
Lot number not given
Catalog No. N1, 200-7

Identity

Ir—The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 3.25 (C-H, aromatic), 4.48 (C≡N), 6.25, 6.75 (C=C, ring), 6.59, 7.46 (N=O), 9.05, 13.39 (C-H), 11.64 (C-N, aromatic NO_2), 7.78, 8.45, 9.85, 14.73 μm.

Nmr—The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 7.90 (doublet, 2H, J_{a-b} = 3.0 cps) H_a

δ 8.38 (doublet, 2H, J_{b-a} = 3.0 cps) H_b.

Uv (Methanol)—λ_{max} = 206.0 nm, A = 1.70, = 9000

λ_{max} = 258.2 nm, A = 2.99, = 15,300.

Purity (>99%)

Elemental Analysis—

Anal. for $C_7H_4N_2O_2$: Calcd: C, 56.76; H, 2.72; N, 18.91

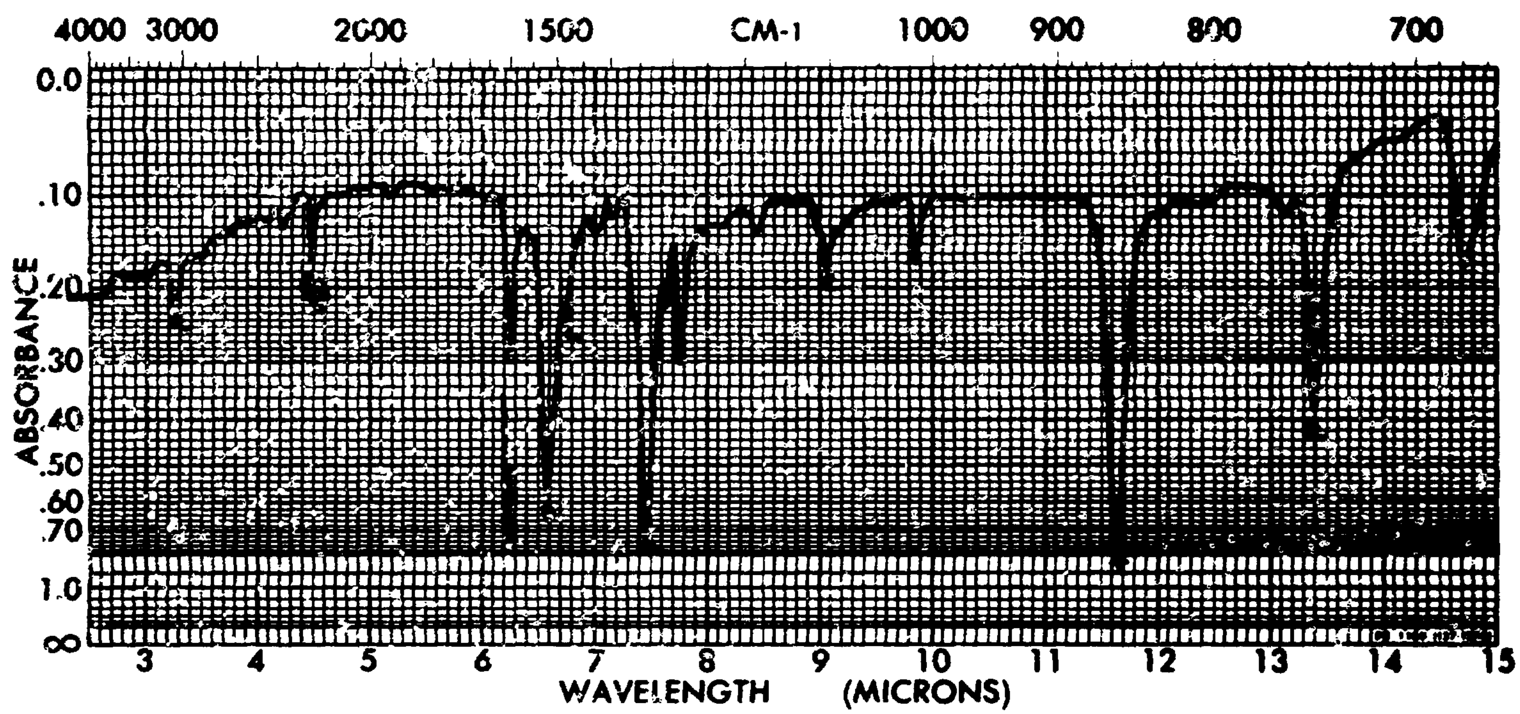
Found: C, 56.52; H, 3.00; N, 18.75.

High-Pressure Liquid Chromatography--One major component (representing 99.5% of total peak areas) and two minor components were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 nm
- Average retention time: 265 sec 4-nitrobenzonitrile 99.5%; 99 sec impurity 0.16%; 189 sec impurity 0.13%.

Gas Chromatography--One major peak (representing 100% of the total peak areas) was observed by gc under the following conditions:

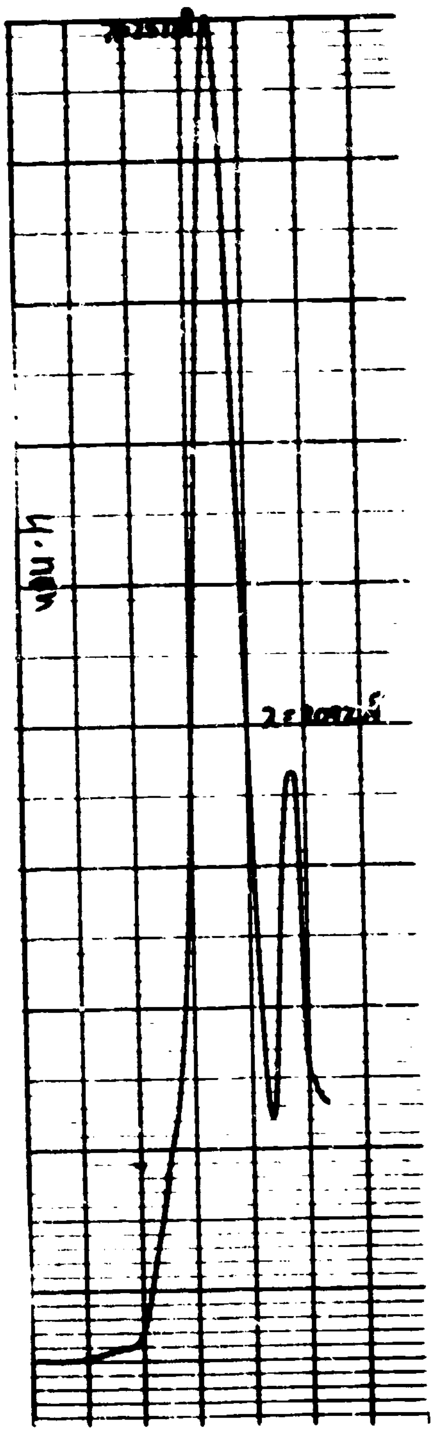
- Column: 6' x 2 mm glass packed with 10% DC 200 on Chromosorb W-HP 80/100.
- Temperature: 130° (4 min) to 220° C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 4.94 min 4-nitrobenzylnitrile 100%.



SPECTRUM NO.	ORIGIN	LEGEND ① C-H, aromatic ② C≡N 1③ C=C, ring ④ N=O ⑤ C-N 2⑥ C-H, aromatic ring	REMARKS
SAMPLE 4-Nitrobenzonitrile			
	PURITY		
	PHASE	DATE 12 April	
	THICKNESS	OPERATOR Keck	

SPECTRUM NO.
SAMPLE

FIGURE 147 INFRARED SPECTRUM OF 4-NITROBENZONITRILE



4-Nitrobenzonitrile

$C = 1.5 \times 10^{-4}\ m/l$

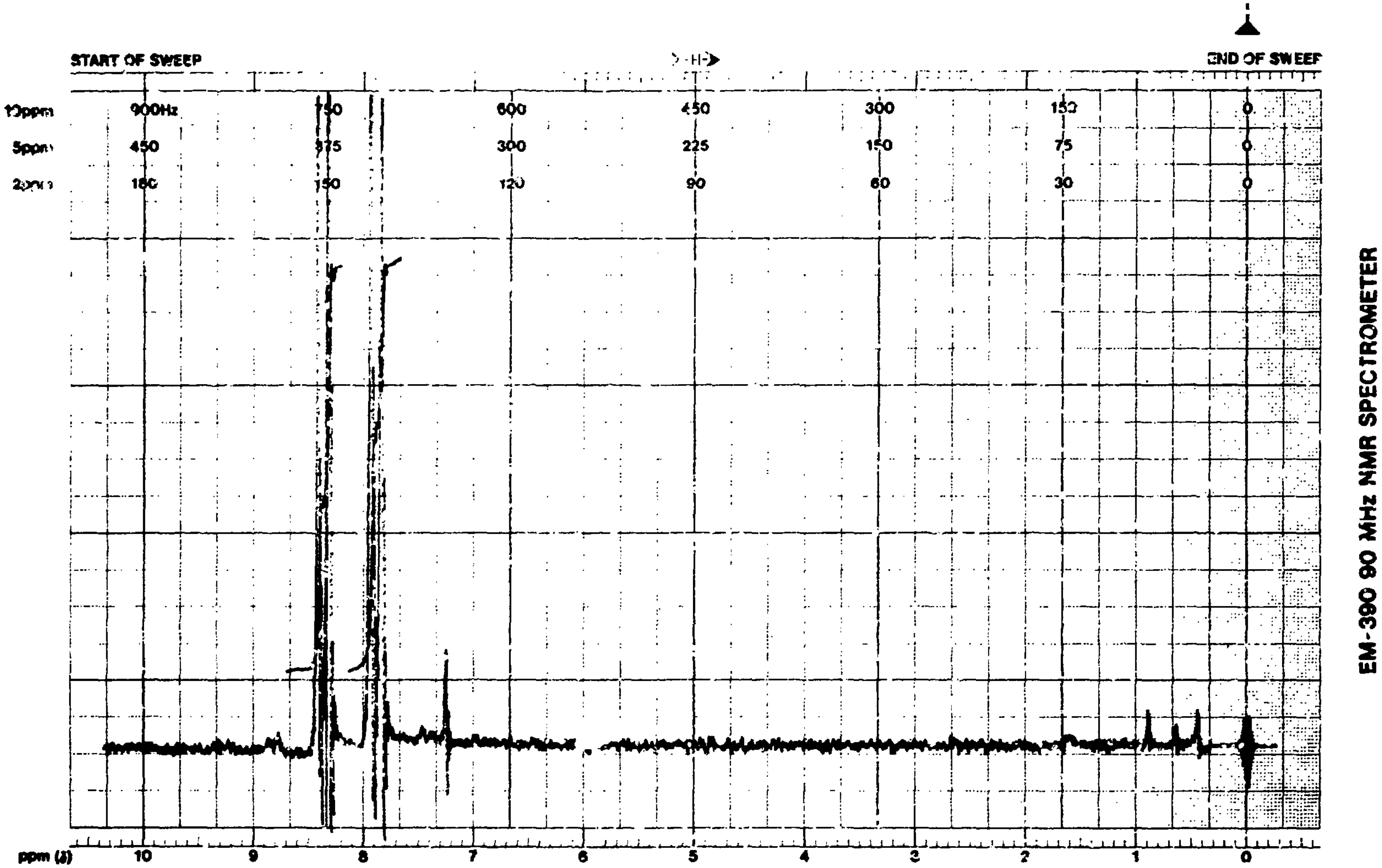
$A_{2677} = 1.845$

$\varepsilon_{2577} = 12300$

$A_{2092} = .760$

$\varepsilon_{2092} = 5067$

FIGURE 148 UV SPECTRUM OF 4-NITROBENZONITRILE



LOCK POS.______ ppm. SPECTRUM AMPL. 5 SWEEP TIME 5 min NUCLEUS ______ SAMPLE: 4-nitrobenzonitrile OPERATOR: KECK

LOCK POWER .002 mG FILTER .05 sec SWEEP WIDTH 10 ppm ZERO REF. ______ DATE 4/10/78

DECOUPLE POS. ______ ppm

DECOUPLING POWER ______ mG RF POWER .04 mG END OF SWEEP ______ ppm SAMPLE TEMP. ______ °C SOLVENT: $CDCl_3$ w/ 1% (v/v) TMS SPECTRUM NO. ______

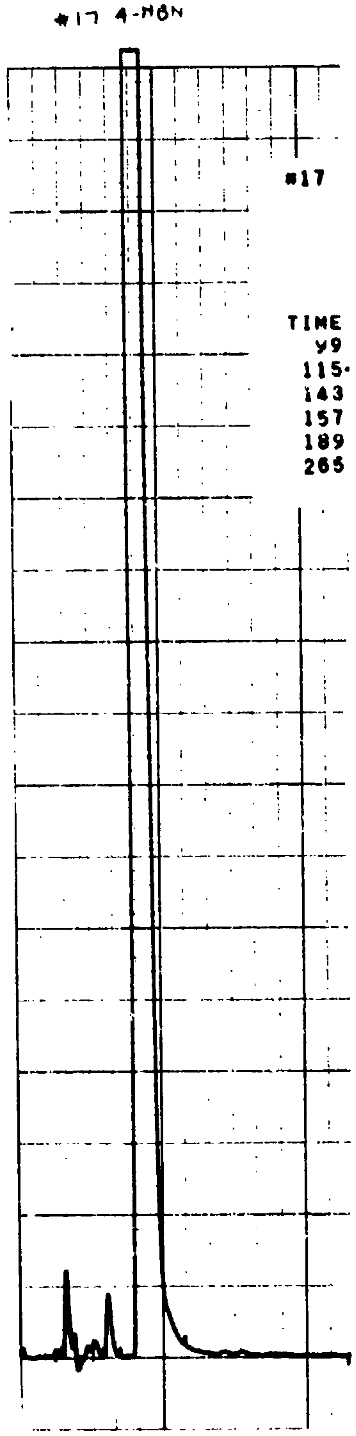
FIGURE 149 NMR SPECTRUM OF 4-NITROBENZONITRILE

varian instrument division palo alto, california

PART NO. [illegible] PRINTED IN U.S.A.

4-NITROBENZONITRILE

HPLC



#17

	10	
	7 PW	
	50 SS	
	5 BL	
	50 TP	
	200 KA	
TIME	AREA	
99	2644 2	0.15 %
115 · SOLVENT	478 2	
143	1265 2	0.0[illegible]
157	1576 3	0.10 %
189	2190	0.13 %
265	1823999	99.53 %
	1832152T	

MAR 2 9 1978

FIGURE 150 HPLC CHROMATOGRAM OF 4-NITROBENZONITRILE

005

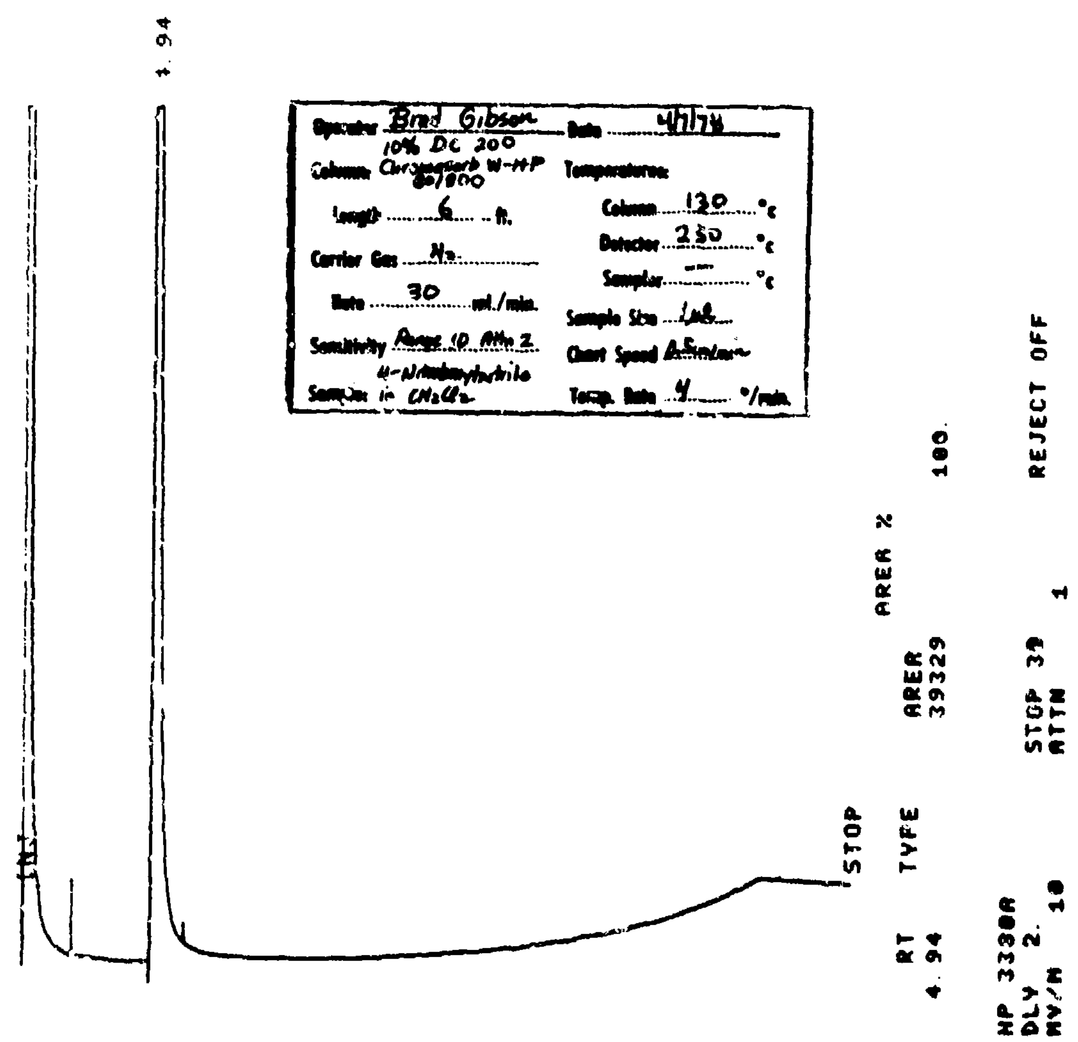


FIGURE 151 GC SPECTRUM OF 4-NITROBENZONITRILE

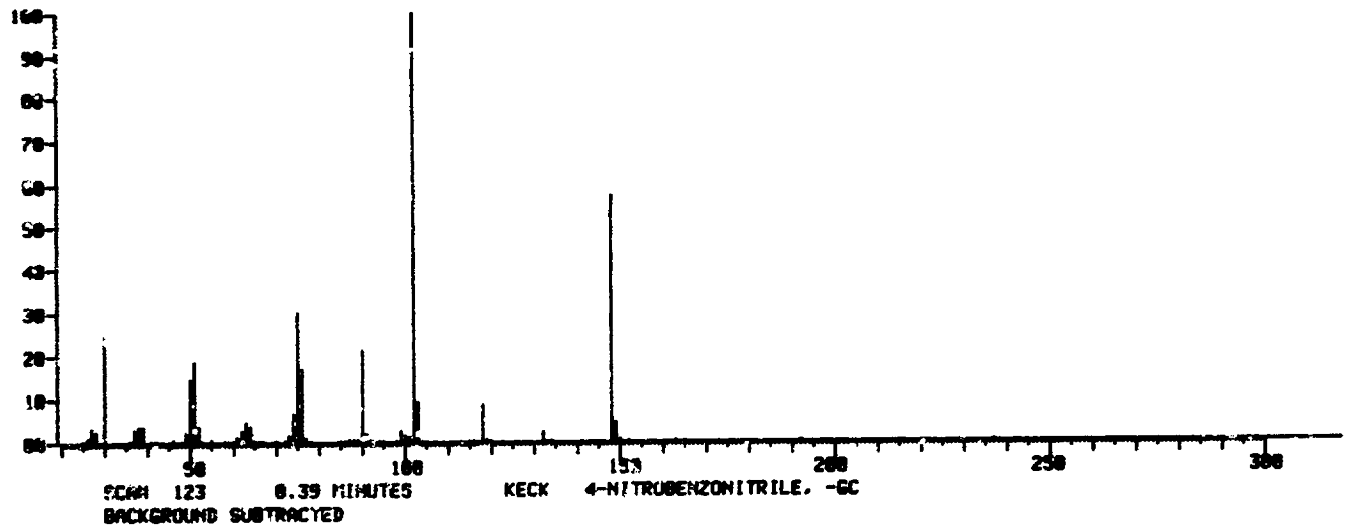
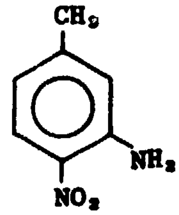
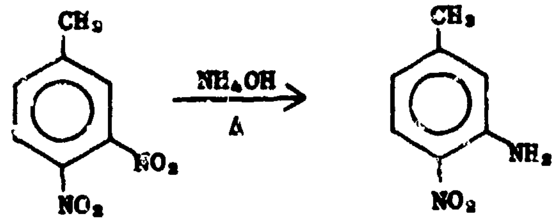


FIGURE 152 MASS SPECTRUM OF 4-NITROBENZONITRILE

4.25 3-Amino-4-Nitrotoluene
5-Methyl-2-nitrobenzenamine



Source: Synthesis, SRI



Identity

Ir—The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 2.85, 2.95 (N-H, 1° aromatic amines), 6.15, 1.75 (C=C ring), 6.30, 7.55 (N=O), 7.08 (C-H, methyl), 8.05 (C-N, 1° aromatic amines), 9.7, 13.3 (C-H), 11.78 (C-N, aromatic NO_2), 8.5, 9.20, 10.5, 12.5, 13.6 μm.

Nmr—The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.25 (singlet, 3H) CH_3

δ 6.00 (singlet, 2H) NH_2

δ 6.45 (doublet, H, J_{a-c} = 3.0 cps) H_a

δ 6.50 (singlet, H) H_b

δ 7.95 (doublet, H, J_{c-a} = 3.0 cps) H_c.

Uv (Methanol)—λ_{max} = 232.4 nm, A = 1.238, ε = 16,150

λ_{max} = 288.3 nm, A = 0.093, ε = 6,300.

Purity (98%)

Elemental Analysis--

Anal. for $C_7H_8N_2O_2$: Calcd: C, 55.26; H, 5.30; N, 18.41
Found: C, 55.09; H, 5.33; N, 18.23.

High-Pressure Liquid Chromatography--One major component (representing 89.8% of total peak areas) and two minor components were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 cm
- Average retention time: 473 sec 3-amino-4-nitrotoluene 89.8%; 239 sec impurity 5.8%; 279 sec impurity 3.6%.

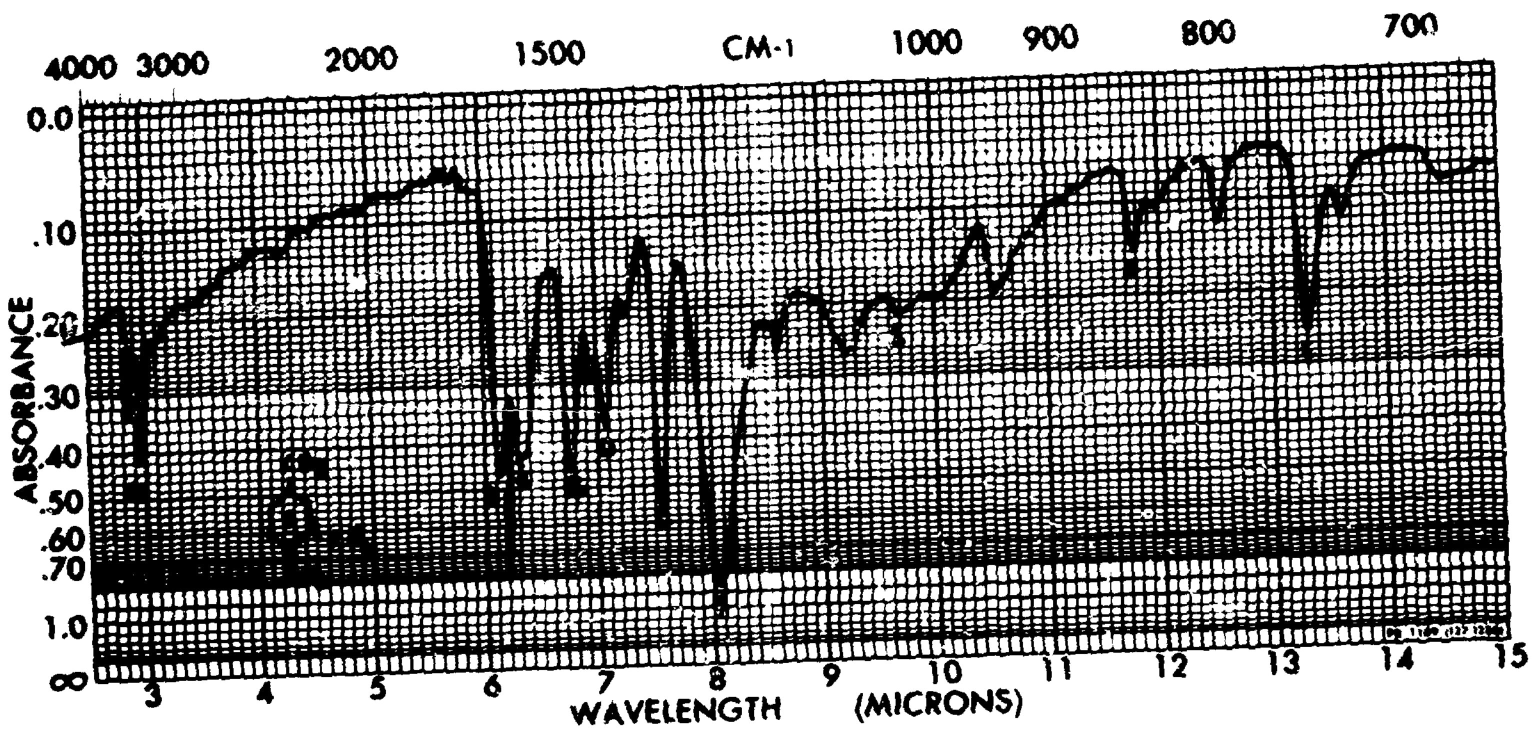
Gas Chromatography--One major component (representing 98.2% of total peak areas) and two minor components, the larger being 4-amino-3-nitrotoluene, were observed by gc under the following conditions:

- Column: 6' x 2 mm glass column packed with 10% DC 200 on Chromasorb W-HP 80/100.
- Temperature: 130° (4 min) to 220° C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 10.30 min 3-amino-4-nitrotoluene 98%; 9.86 min 4-amino-3-nitrotoluene 1.8%; 3.2 min impurity 0.2%.

Gas Chromatography--One major component (representing 98% of total peak areas) and two minor components, the larger being 4-amino-3-nitrotoluene, were observed by gc under the following conditions:

- Column: 60-m SE30 glass capillary; Supelco
- Temperature: 130° (2 min) to 210° C at 2°/min
- Flow rate: 0.5 ml/min N_2

- **Split ratio: 150/1**
- **Detection: Flame ionization**
- **Retention time: 22.61 min 3-amino-4-nitrotoluene 98%; 21.44 min 4-amino-3-nitrotoluene 1.7%; 11.00 min impurity 0.3%.**



SPECTRUM NO.

SAMPLE 3-amino-4-Nitrotoluene

KBr Pellet

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND ① n-H, 1° aromatic amines

② C=C ring

③ N=O

④ C-n, 1° aromatic amine

⑤ C-H

⑥ C-H, CH_3

2.⑦ C-n, aromatic NO_2

DATE 17 April 78

OPERATOR Keck

REMARKS

SPECTRUM NO.

SAMPLE

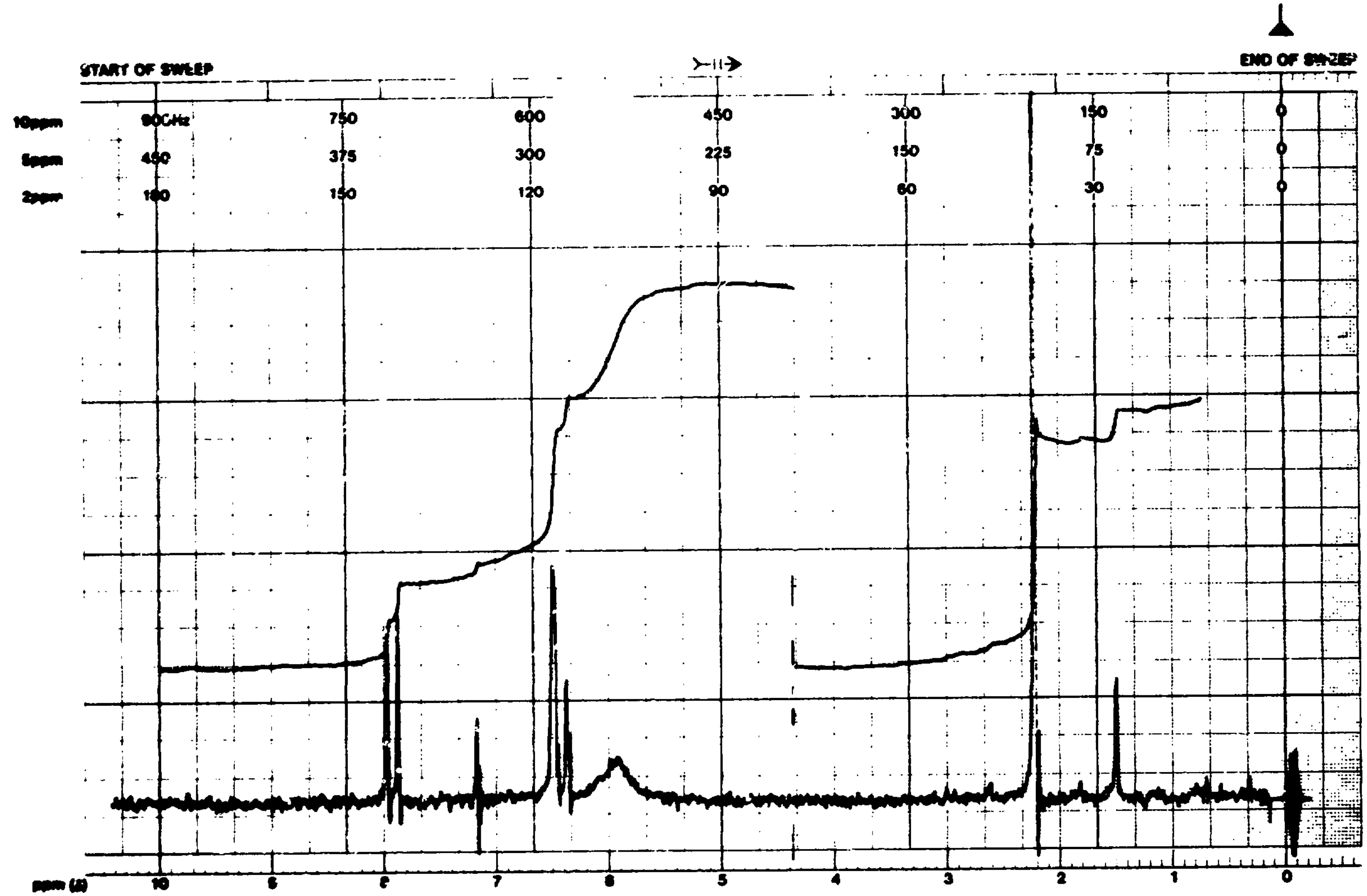
RECORDING CHARTS

GRAPHIC CONTROLS CORPORATION

BUFFALO NEW YORK

PRINTED IN U.S.A.

FIGURE 153 INFRARED SPECTRUM OF 3-AMINO-4-NITROTOLUENE



EM-390 90 MHz NMR SPECTROMETER

LOCK POS. ______ ppm
LOCK POWER .002 mG
DECOUPLE POS. ______ ppm
DECOUPLING POWER ______ mG

SPECTRUM AMPL. 5
FILTER .05 sec
RF POWER .04 mG

SWEEP TIME 5 min
SWEEP WIDTH 10 ppm
END OF SWEEP ______ ppm

NUCLEUS ______
ZERO REF. ______
SAMPLE TEMP. ______ °C

SAMPLE: 3-Amino-4-nitrotoluene
SOLVENT: $CDCl_3$ w/ 1% (v/v) TMS

OPERATOR KECK
DATE 4/10/78
SPECTRUM NO. ______

FIGURE 154 NMR SPECTRUM OF 3-AMINO-4-NITROTOLUENE

varian instrument division palo alto, california

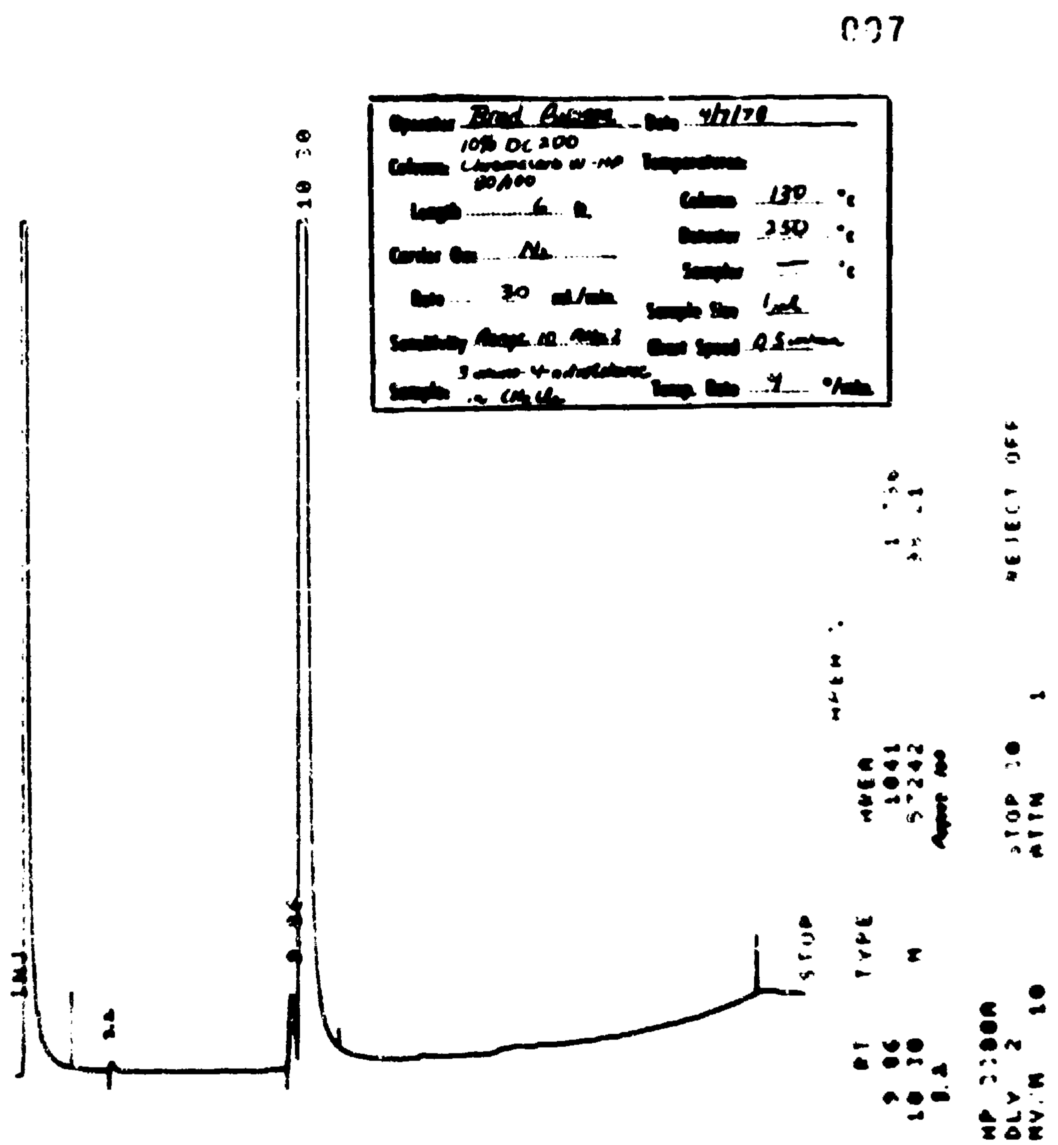


FIGURE 155 GC SPECTRUM OF 3-AMINO-4-NITROTOLUENE

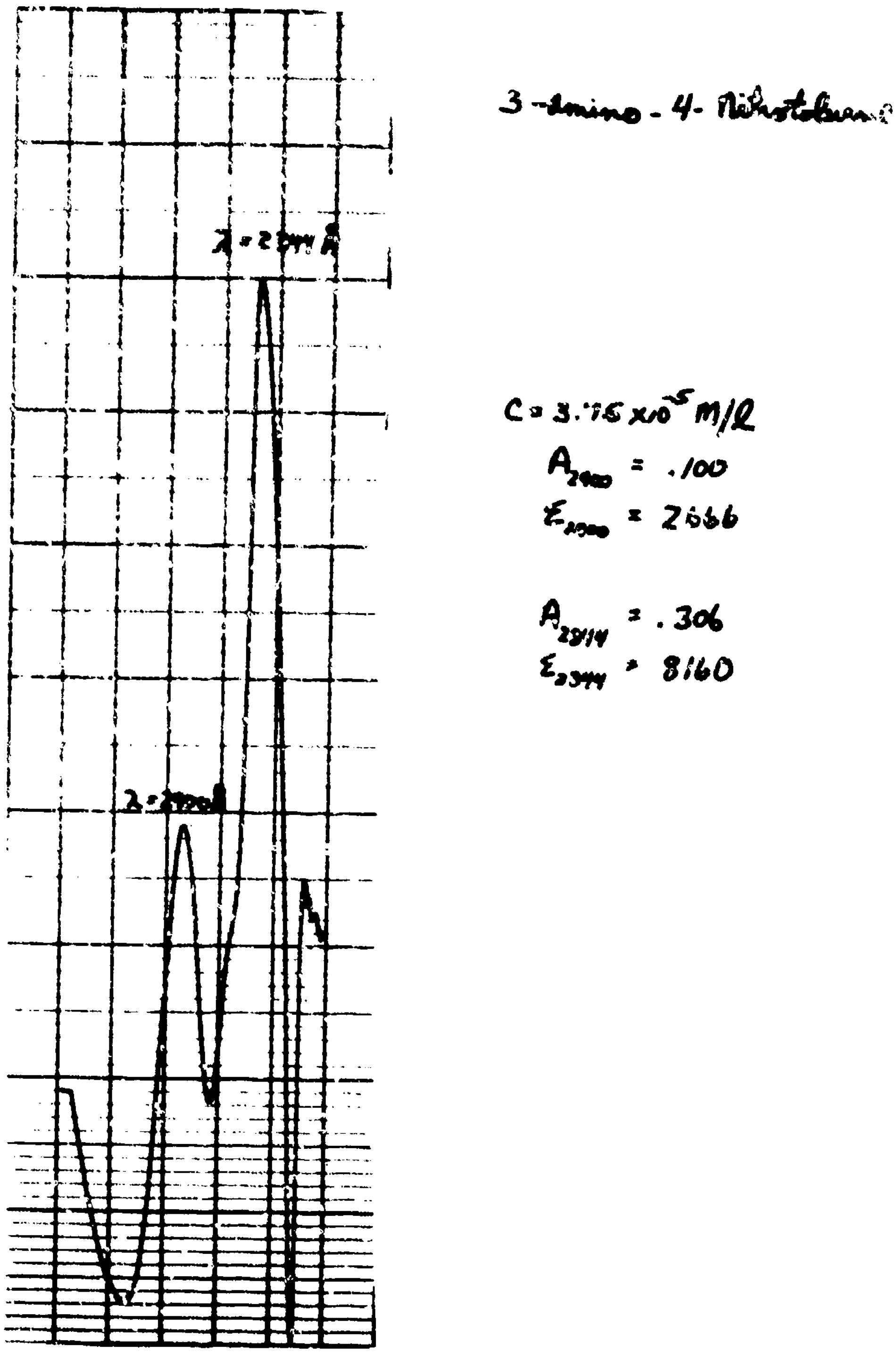
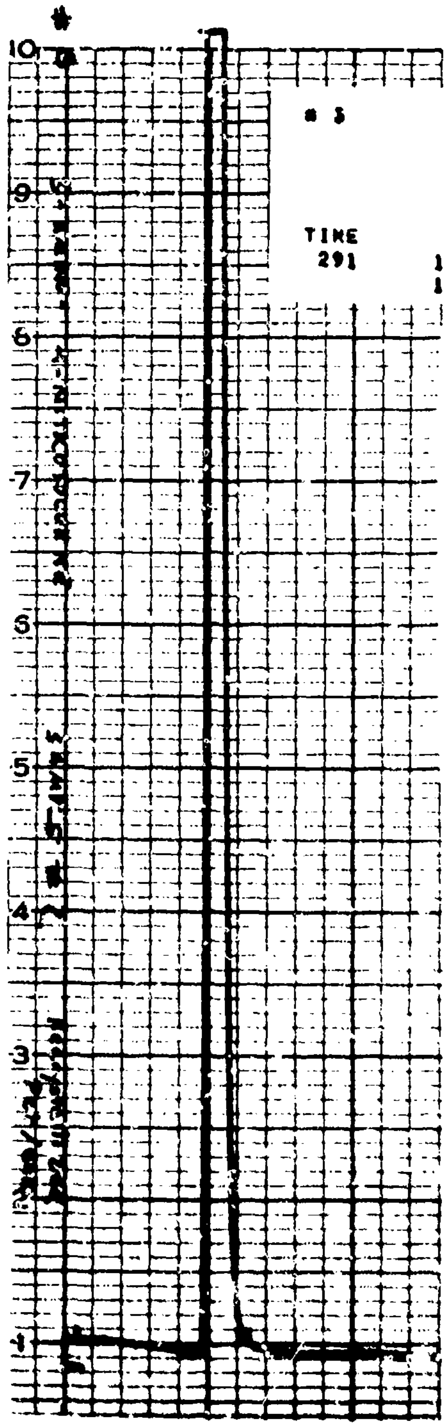


FIGURE 156 UV SPECTRUM OF 3-AMINO-4-NITROTOLUENE

3- AMINO - 4- NITROTOLUENE SAMPLE #2

Recrystallized Pet/Cnlo

HPLC



COLUMN: μ Bondapak C_{18} 3.9 mm X 30 cm

SOLVENT: 60% MeOH / 40% H_2O

FLOW RATE: 1.8 ml/min

DETECTION: UV at 254 nm

FIGURE 157 HPLC CHROMATOGRAM OF 3-AMINO-4-NITROTOLUENE

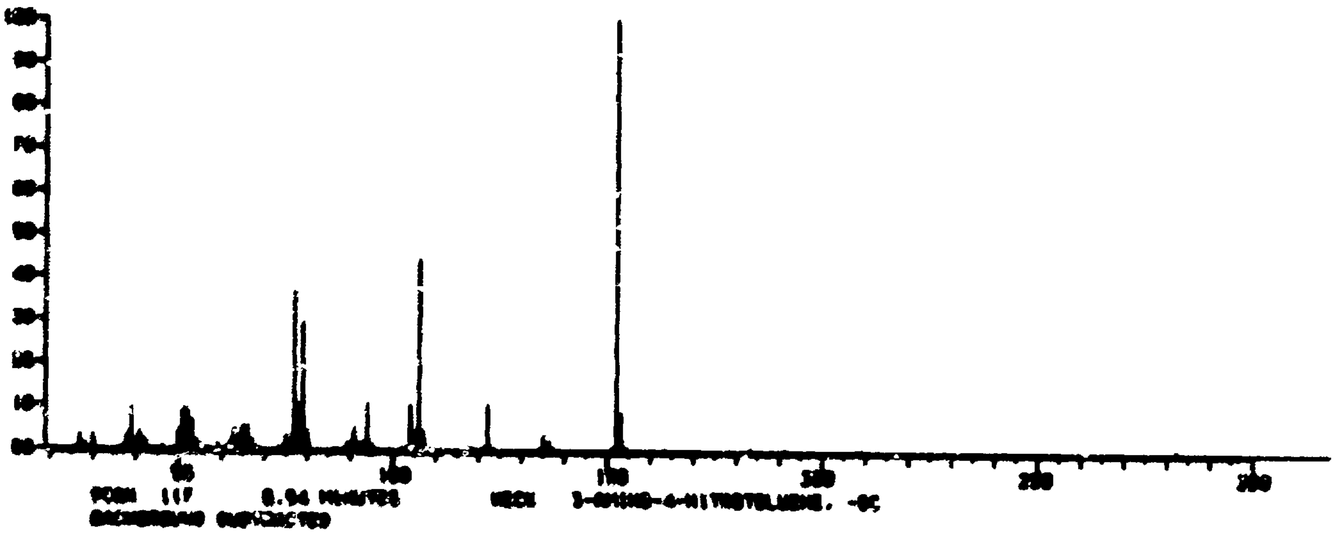
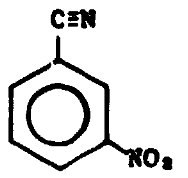


FIGURE 158 MASS SPECTRUM OF 3-AMINO-4-NITROTOLUENE

4.26 3-Nitrobenzonitrile
[619-24-9]



Source: Aldrich Chemical Company
Lot No. 090357CB
Catalog No. 16,774-6

Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 3.25 (C-H, aromatic), 4.45 (C≡N), 6.19, 6.80 (C=C, ring), 6.55, 7.43 (N=O), 9.1, 13.64 (C-H), 12.25 (C-N, aromatic NO_2), 8.35, 9.30, 10.85, 11.05, 12.69 nm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals: δ 7.73 (triplet, H, J_{a-bc} = 2.5 cps) H_a
δ 8.03 (doublet of triplets, H, J_{b-a} = 2.0 cps) H_b
δ 8.50 (doublet of triplets, H, J_{c-a} = 2.0 cps) H_c
δ 8.56 (singlet, H) H_d.

Uv (Methanol)--λ_{max} = 216.2 nm, A = 0.513, ε = 34,200
λ_{max} = 252.1 nm, A = 0.144, ε = 9600

Purity (>99%)

Elemental Analysis--

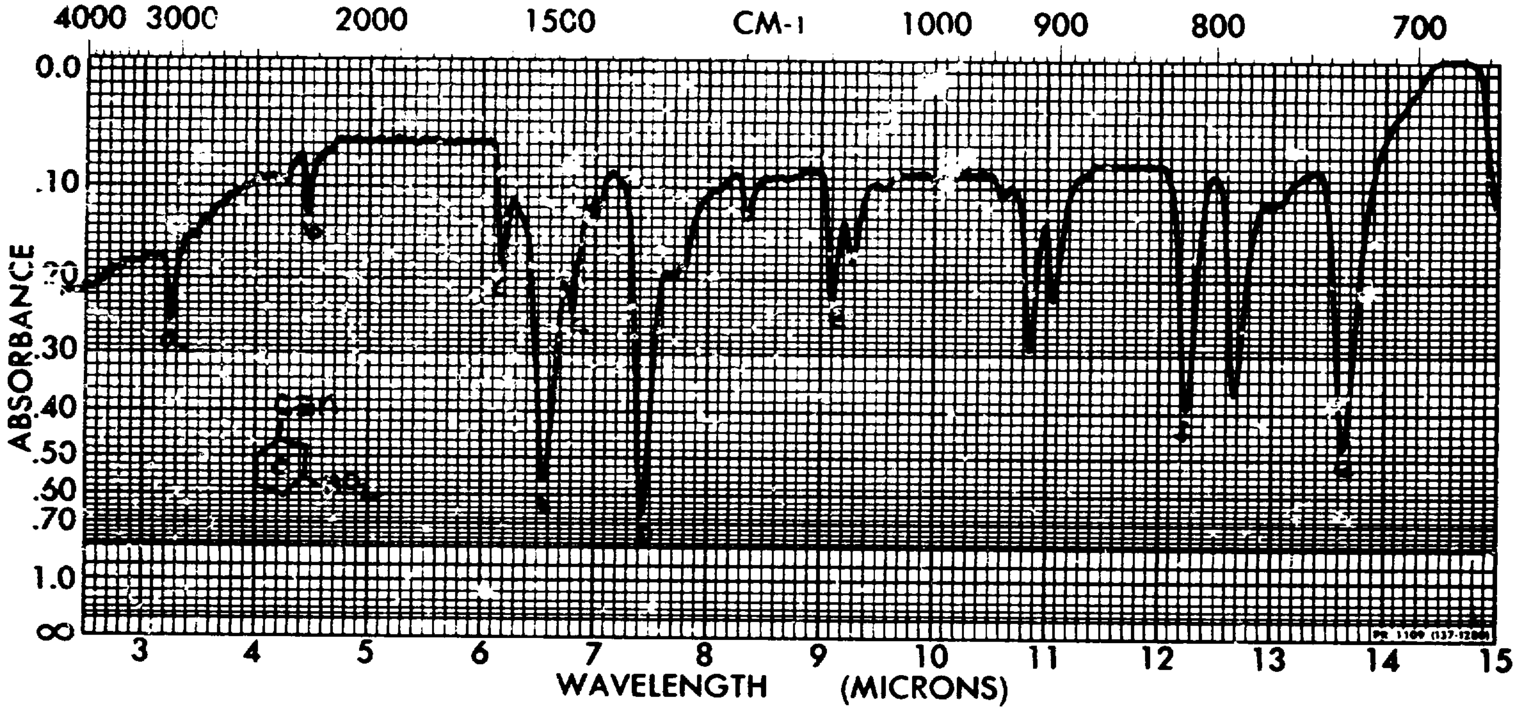
Anal. for $C_7H_4N_2O_2$: Calcd: C, 56.76; H, 2.72; N, 18.91
Found: C, 56.54; H, 2.83; N, 18.82.

<u>High-Pressure Liquid Chromatography</u>--One major component (representing 99.8% of total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% MeOH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 nm
- Average retention time: 281 sec 3-nitrobenzonitrile 99.8%; 470 sec impurity 0.11%.

<u>Gas Chromatography</u>--One major peak (representing 100% of the total peak areas) was observed by gc under the following conditions:

- Column: 6' x 2 mm glass column packed with 10% DC 200 on Chromasorb W-HP 80/100.
- Temperature: 130° (4 min) to 220° C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 5.20 min 3-nitrobenzylnitrile 100%.



SPECTRUM NO.	ORIGIN	LEGEND ⓐ C-H, aromatic ⓑ C≡N 1. ⓒ C=C ⓓ N=O ⓔ C-N 2. ⓕ C-H, aromatic NO_2	REMARKS
SAMPLE 3-Nitrobenzonitrile			
	PURITY		
	PHASE	DATE 13 April 78	
	THICKNESS	OPERATOR Keck	

SPECTRUM NO.
SAMPLE

FIGURE 159 INFRARED SPECTRUM OF 3-NITROBENZONITRILE

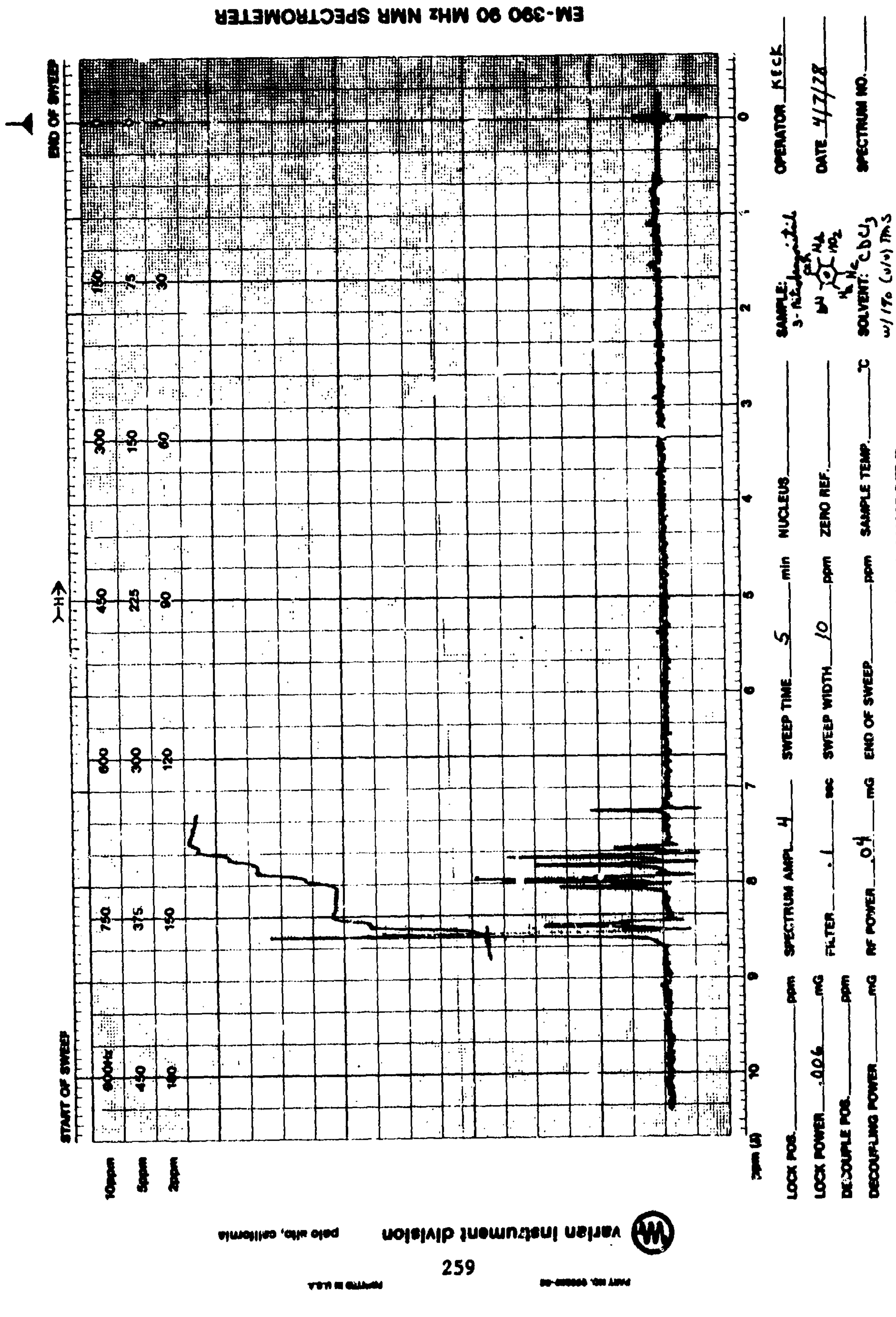


FIGURE 160 NMR SPECTRUM OF 3-NITROBENZONITRILE

004

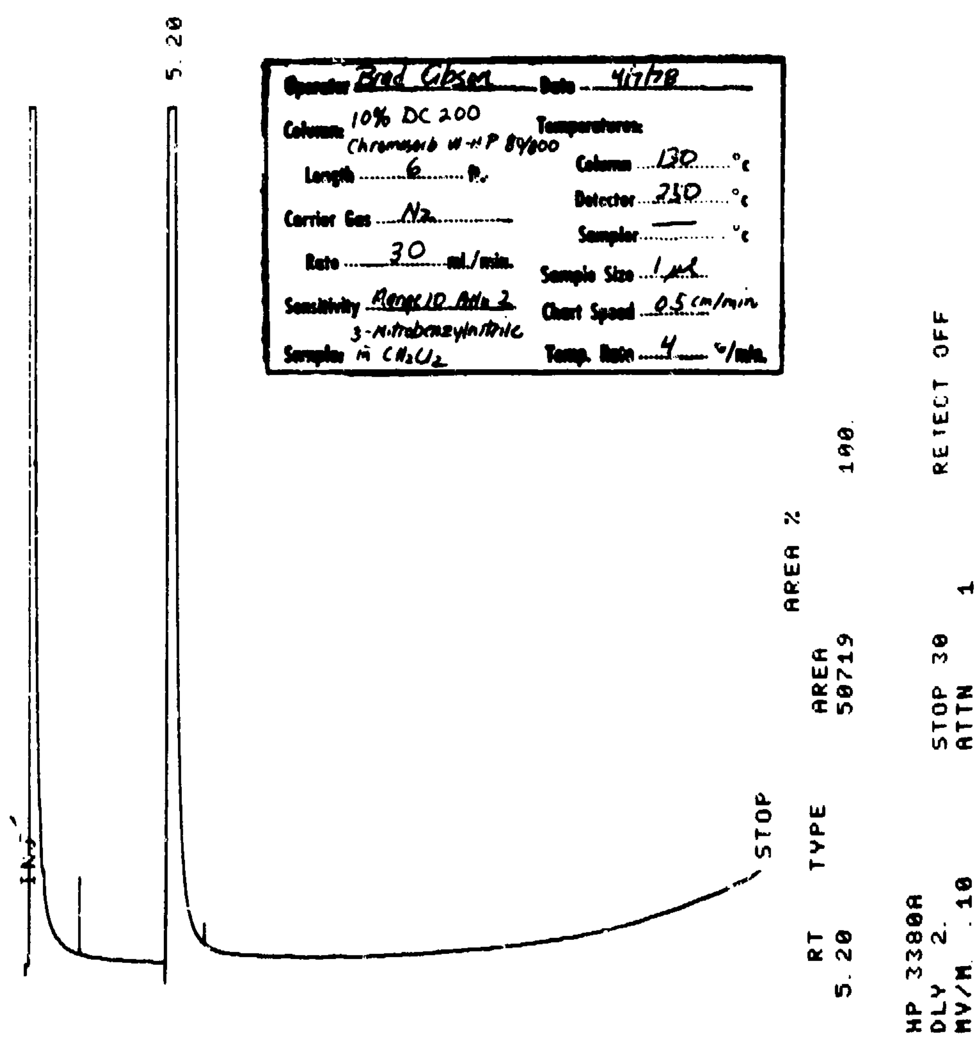
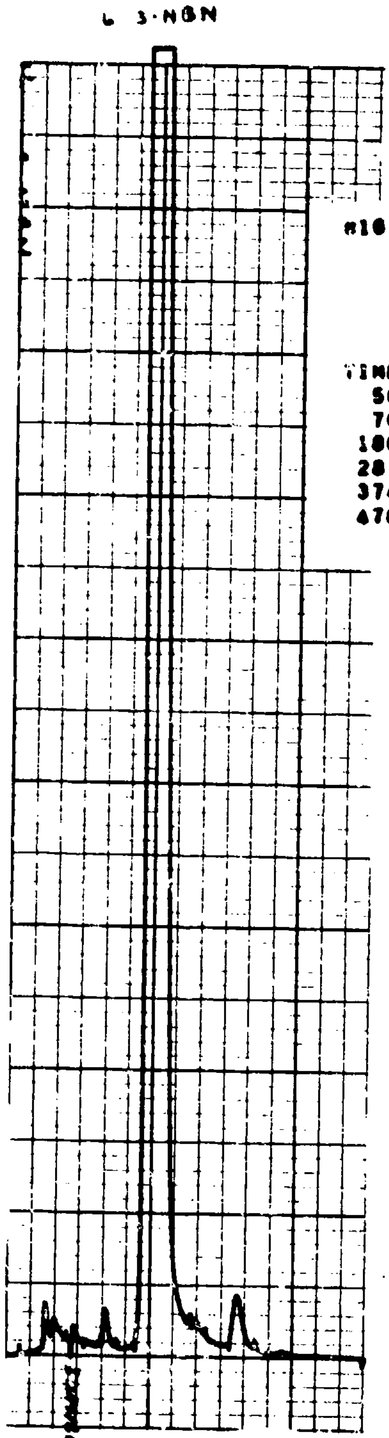


FIGURE 161 GC SPECTRUM OF 3-NITROBENZONITRILE

3-NITROBENZONITRILE

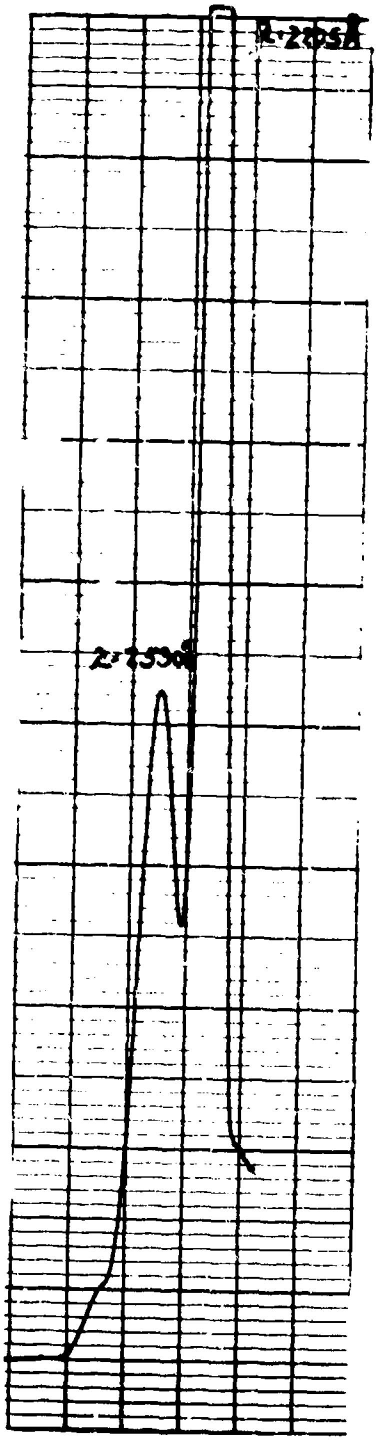
HPLC



#16	10	
	7 PW	
	50 SS	
	5 AL	
	60 TP	
	200 MA	
TIME	AREA	
56	1330 2	0.04%
76	1030 2	0.03%
186	1316	0.04%
281	3195435	99.77%
374	300	0.01%
470	3490	0.11%
	3202901T	

MAR 29 1978

FIGURE 162 HPLC CHROMATOGRAM OF 3-NITRO[illegible]ONITRILE



3-Nitrobenzonitrile

$C = 1.4 \times 10^{-4}$ m/l

A = .880

= 6286

A_{2205} = 2.58

ε_{2205} = 18429

FIGURE 163 UV SPECTRUM OF 3-NITROBENZONITRILE

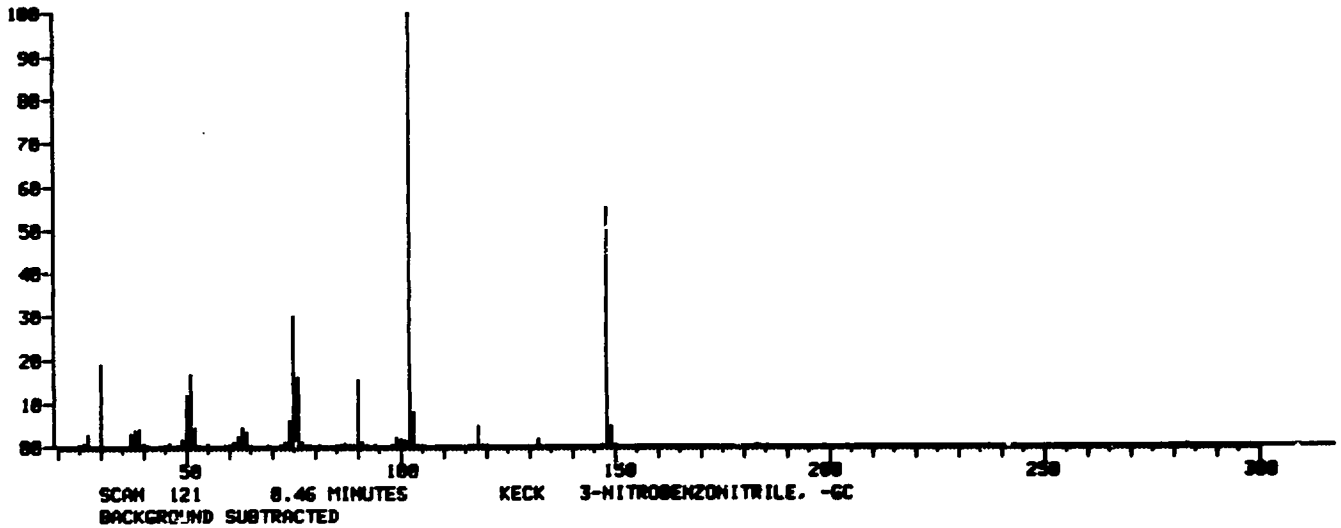
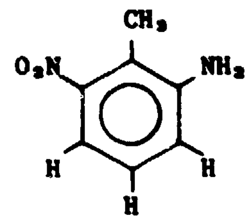


FIGURE 164 MASS SPECTRUM OF 3-NITROBENZONITRILE

4.27 2-Amino-6-Nitrotoluene

2-Methyl-3-nitrobenzenamine
[603-83-8]



Source: Aldrich Chemical Company
Lot No. 031207
Catalog No. 11,584-3

Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 3.2 (N-H, 1° aromatic amines), 6.2 (C=C ring), 6.65, 7.45 (N=O), 7.6 (C-N, 1° aromatic amines), 9.68, 13.75 (C-H), 11.25 (C-N, aromatic NO_2), 6.1, 7.8, 8.95, 12.68 µm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed and the number of protons each signal represents was determined from signal integrals:

δ 2.23 (singlet, 3H) CH_3
δ 3.92 (singlet, 2H) NH_2
δ 6.75-6.95 (multiplet, H)
δ 7.0-7.2 (multiplet, 2H).

Uv (Methanol)--λ_{max} = 206.1 nm, A = 0.125, ε = 15,000
λ_{max} = 234.4 nm, A = 0.124, ε = 14,800
λ_{max} = 350.0 nm, A = 0.125, ε = 480.

Purity (99%)

Elemental Analysis--

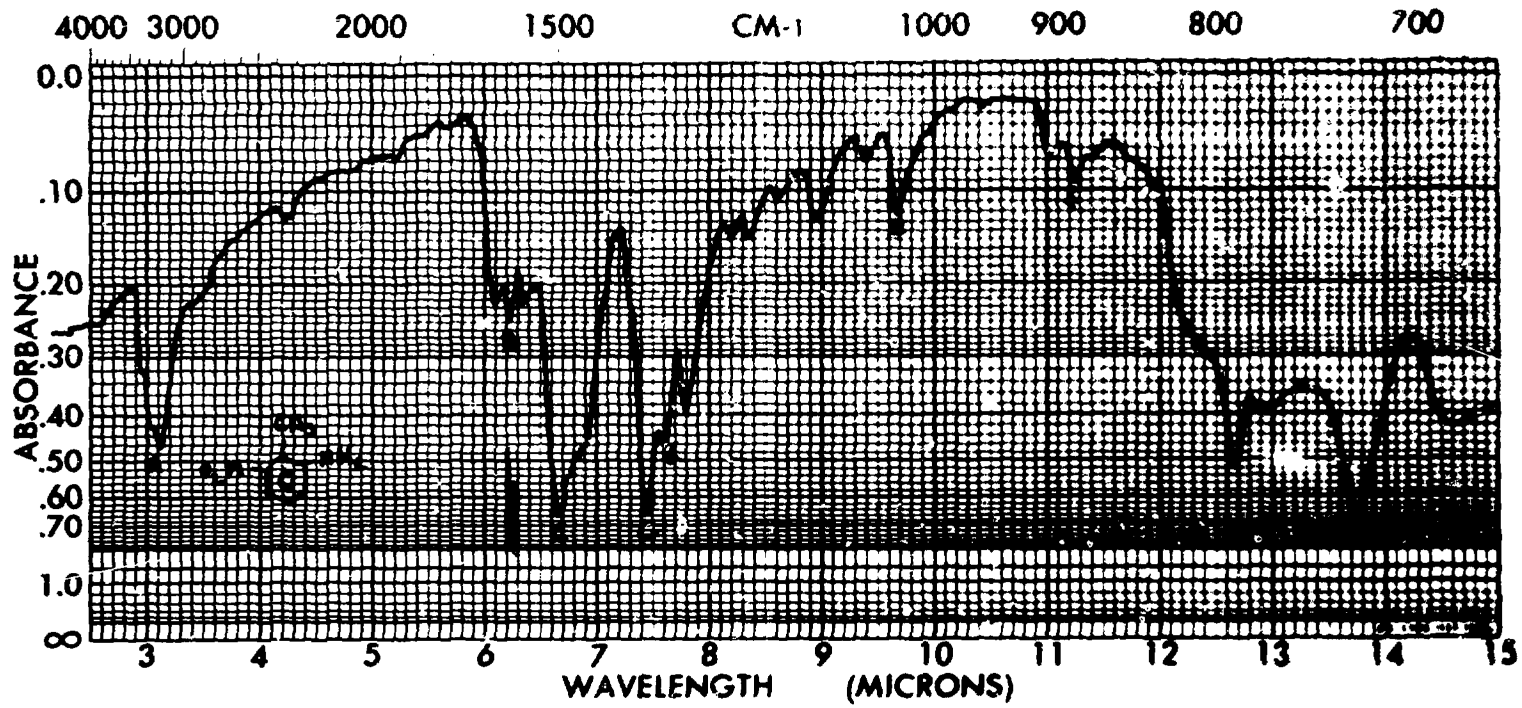
Anal. for $C_7H_8N_2O_2$: Calcd: C, 55.26; H, 5.30; N, 18.41
Found: C, 55.09; H, 5.33; N, 18.23.

High-Pressure Liquid Chromatography--One peak representing 100% of total peak areas was observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 60% H_2O/40% CH_3OH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 nm
- Average retention time: 353 sec 2-amino-6-nitrotoluene 100%.

Gas Chromatography--One major peak (representing 99.8% of total peak areas) and two minor peaks were observed by gc under the following conditions:

- 60-m SE 30 g ass capillary; Supelco
- Temperature: 150° to 220° C at 2°/min
- Flow rate: 0.5 ml/min
- Split ratio: 150/1
- Detection: Flame ionization
- Retention time: 17.66 min 2-amino-6-nitrotoluene 99.8%; 18.47 min impurity 0.1%; 19.3 min impurity 0.1%.



SPECTRUM NO.	ORIGIN	LEGEND ① N-H, 1° aromatic amine ① C=C ring ① N=O 1. ① C-N, 1° aromatic amine ① C-N ① C-N, aromatic NO_2 2.	REMARKS
SAMPLE 2-amino-6-nitrotoluene	PURITY		
	PHASE	DATE 17 April 78	
	THICKNESS	OPERATOR Keck	

SPECTRUM NO.
SAMPLE

FIGURE 165 INFRARED SPECTRUM OF 2-AMINO-6-NITPOTOLUENE

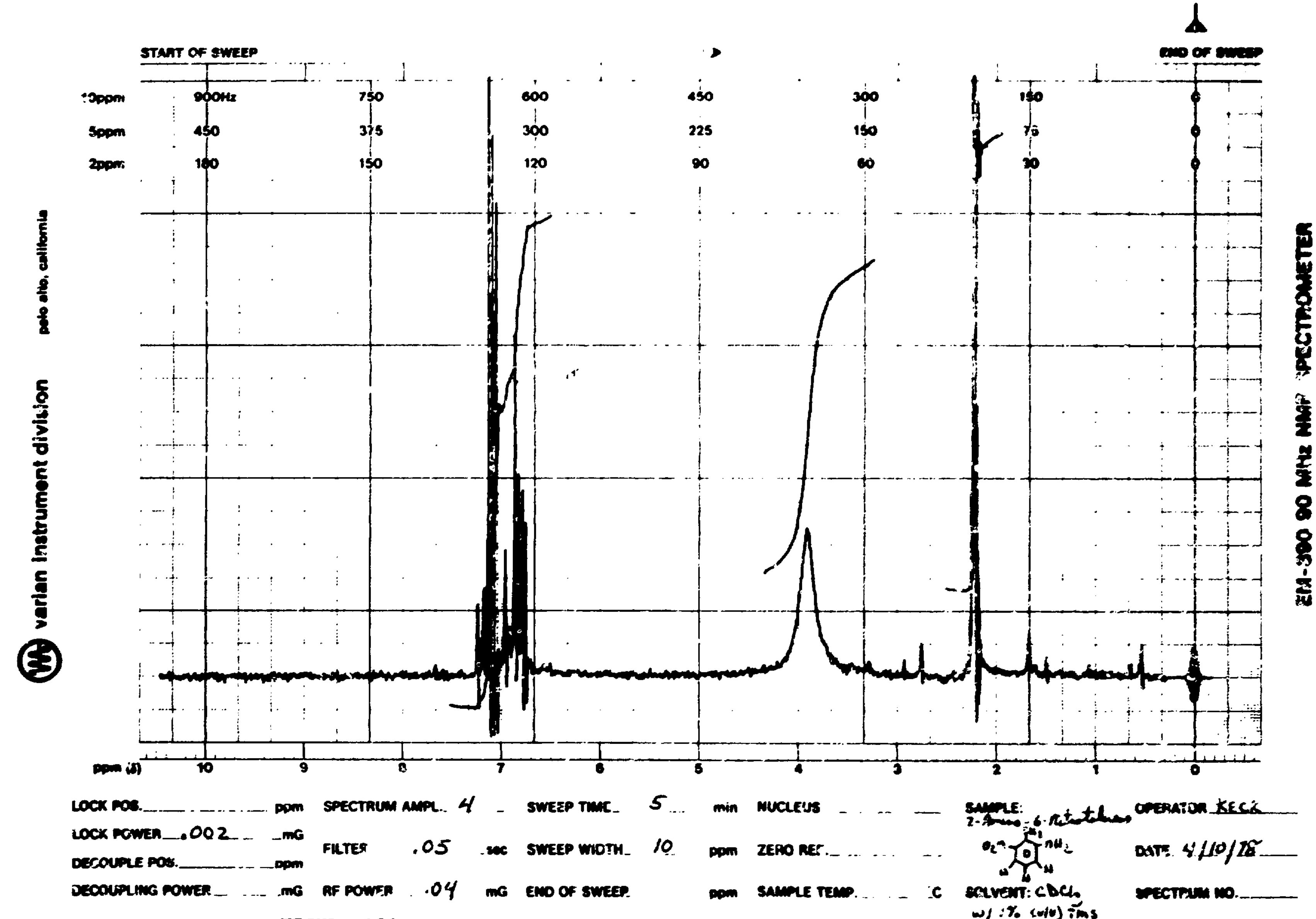
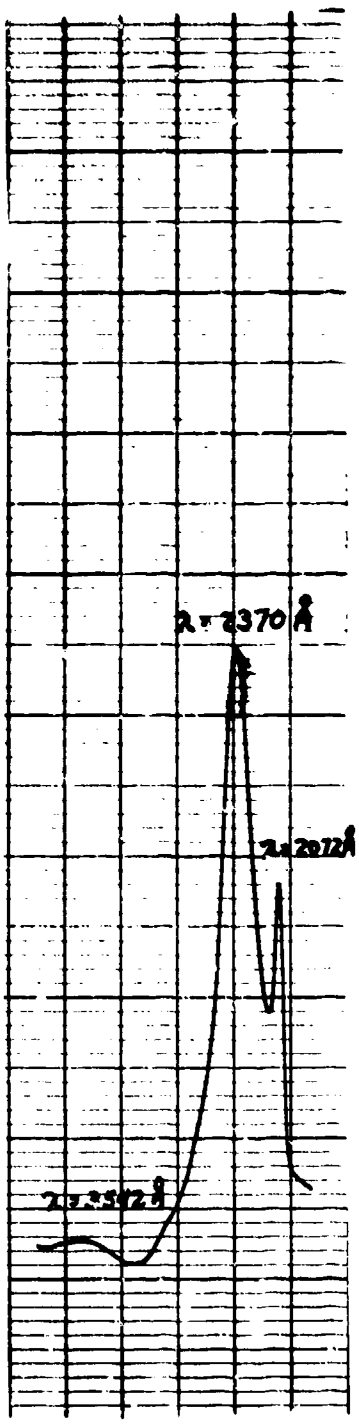


FIGURE 166 NMR SPECTRUM OF 2-AMINO-6-NITROTOLUENE



2-amino-6-nitrotoluene

$C = 1.7 \times 10^{-4}$ M/l

$A_{2842} = .14$

$\varepsilon_{2842} = 824$

$A_{2370} = 2.26$

$\varepsilon_{2370} = 13294$

$A_{2072} = 1.42$

$\varepsilon_{2072} = 8353$

FIGURE 167 UV SPECTRUM OF 2-AMINO-6-NITROTOLUENE

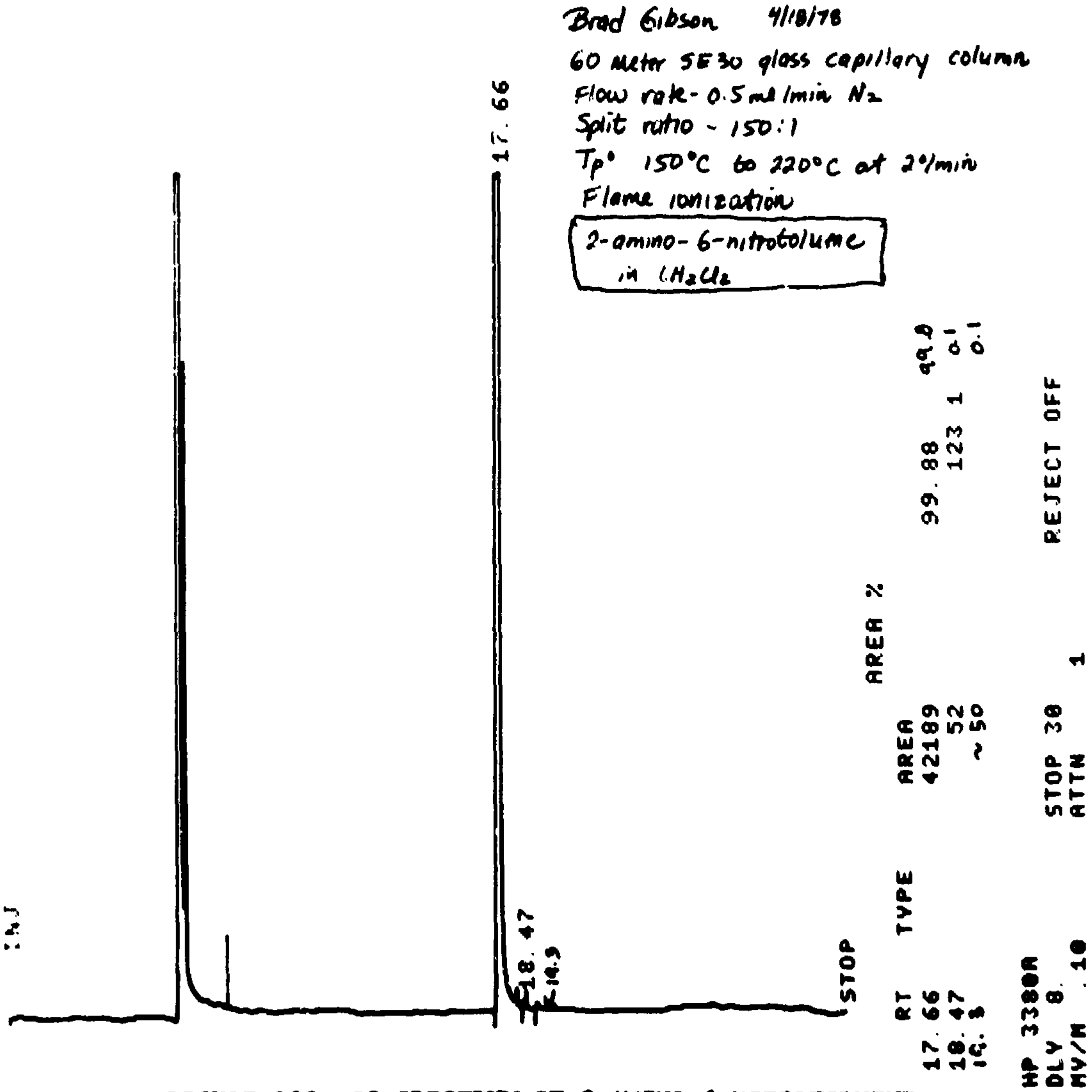


FIGURE 168 GC SPECTRUM OF 2-AMINO-6-NITROTOLUENE

2-AMINO-6-NITROTOLUENE

HPLC CONDITIONS:

COLUMN: µ BONDAPAK C_{18}
SOLVENT: 40% CH_3OH / 60% H_2O
FLOW RATE: 2.0 ml/min
DETECTION: UV at 254 nm

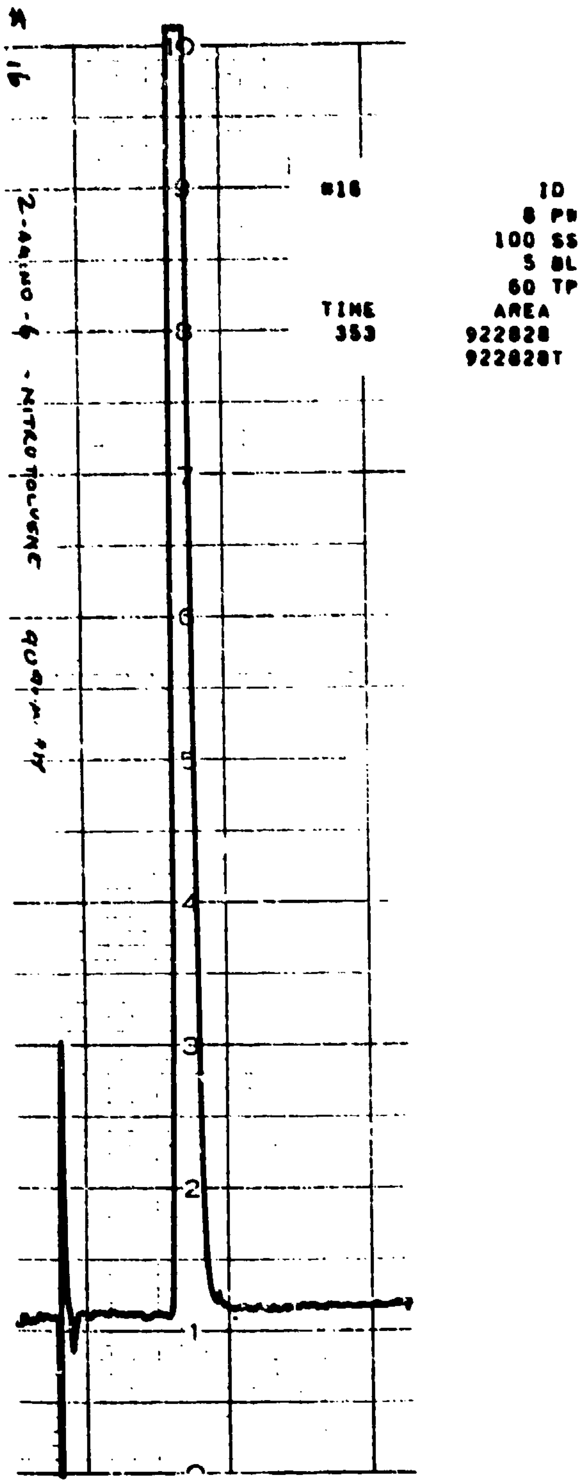


FIGURE 169 HPLC CHROMATOGRAM OF 2-AMINO-6-NITROTOLUENE

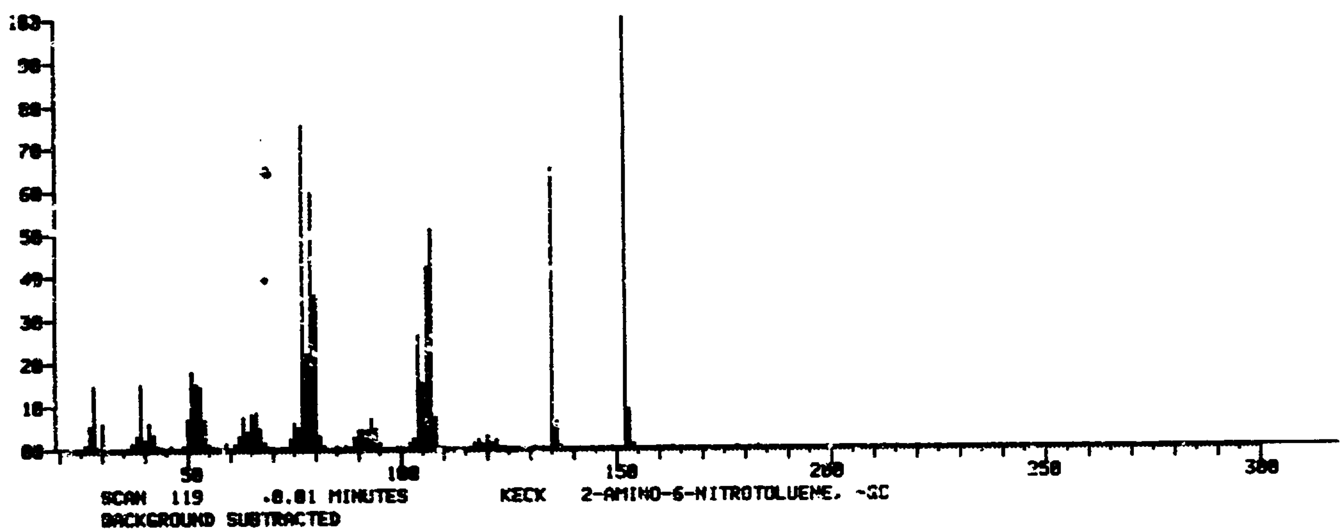
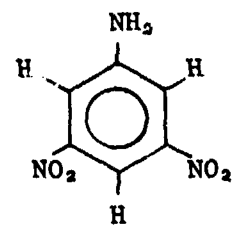


FIGURE 170 MASS SPECTRUM OF 2-AMINO-6-NITROTOLUENE

4.28 3,5-Dinitroaniline
3,5-Dinitrobenzenamine
[618-87-1]



Source: Aldrich Chemical Company
Lot No. 011477AB
Catalog No. 019,340-2

Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 2.85, 2.95 (N-H, 1° aromatic amines), 3.25 (C-H, aromatic), 6.18, 6.9 (C=C, ring), 6.6 (N=O), 7.5 (C-N, 1° aromatic amines), 9.15, 13.72 (C-H), 11.38 (C-N, aromatic NO_2), 10.02, 10.8, 12.35 μm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed and the number of protons each signal represents was determined from signal integrals:

δ 4.35 (singlet, 2H) NH_2
δ 7.68 (doublet, 2H, J_{a-b} = 0.8 cps) H_a
δ 8.30 (triplet, H, J_{b-a} = 0.8 cps) H_b.

Uv (Methanol)--λ_{max} = 228.2 nm, A = 0.114, ε = 22330
λ_{max} = 258.0 nm, A = 0.053, ε = 10380.

Purity (98%)

Elemental Analysis

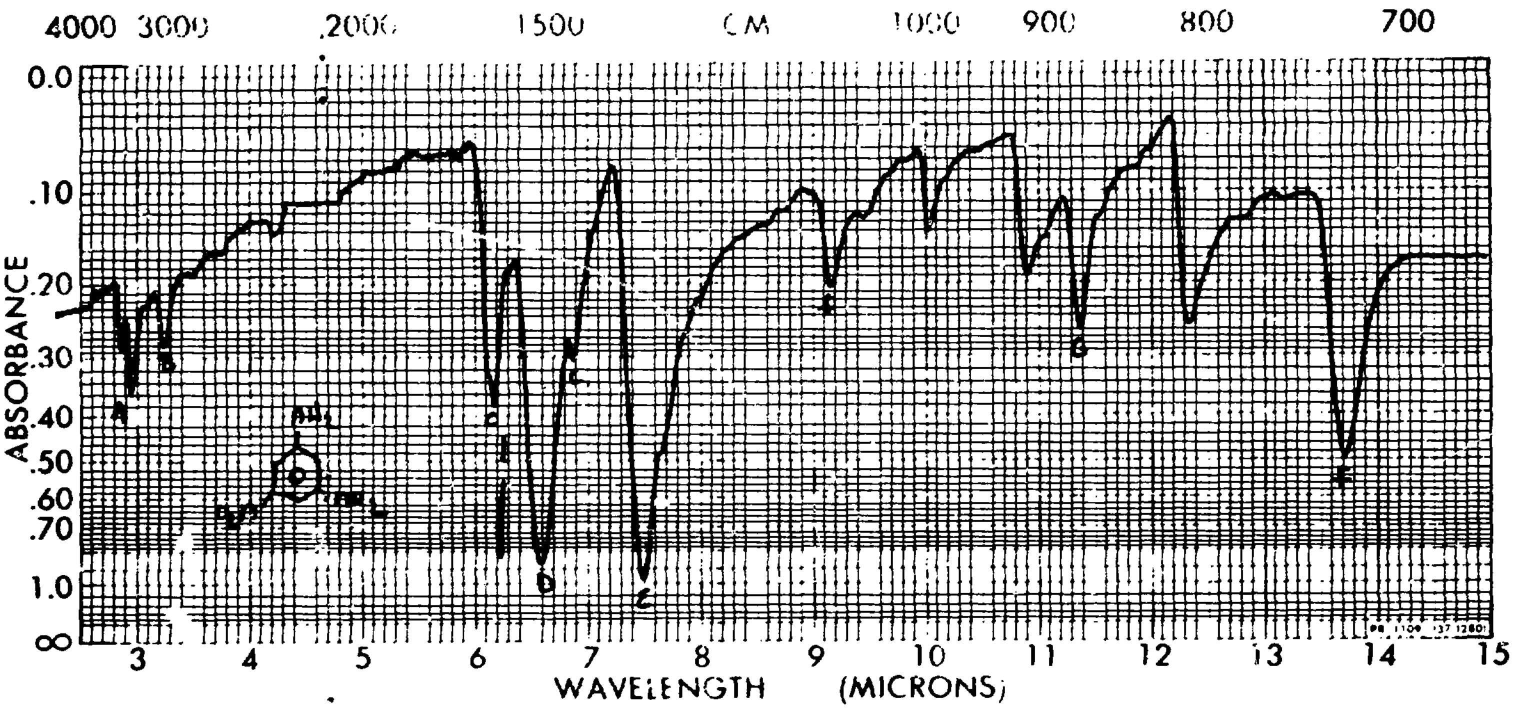
Anal. for $C_6H_5N_3O_4$: Calcd: C, 39.35; H, 2.75; N, 22.95
Found: C, 39.48; H, 2.83; N, 22.50.

High-Pressure Liquid Chromatography--One major component (representing 99.8% of the total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 nm
- Average retention time: 414 sec 3,5-dinitroaniline 99.8%; 242 sec impurity 0.2%.

Gas Chromatography--One major peak (representing 100% of total peak areas) was observed by gc under the following conditions:

- Column: 6' x 2 mm glass column packed with 10% DC200 on Chromasorb W-HP.
- Temperature: 130° (4 min) to 220° C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention Time: 20.13 min 3,5-dinitroaniline 100%.



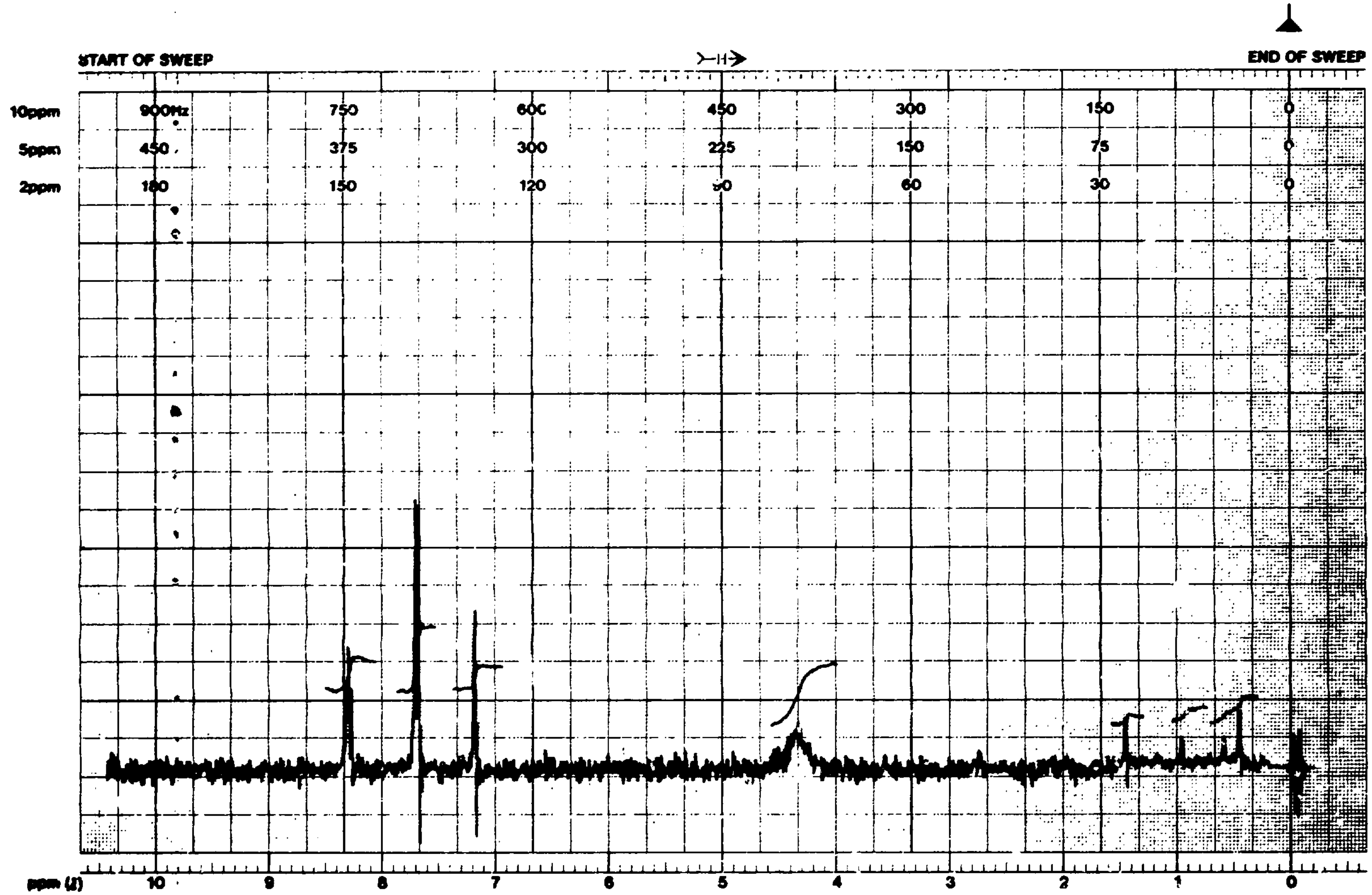
SPECTRUM NO. SAMPLE 3,5-Dinitroaniline	ORIGIN PURITY PHASE THICKNESS	LEGEND: A N-H, 1° aromatic amine B C-H, aromatic C C=C ring D N=O E C-N, 1° aromatic amine F C-H G C-N, aromatic NO_2 DATE 17 April 78 OPERATOR KECK	REMARKS

SPECTRUM NO.
SAMPLE

RECORDING CHARTS

FIGURE 171 INFRARED SPECTRUM OF 3,5-DINITROANILINE

EM-390 90 MHz NMR SPECTROMETER



LOCK POS.______ ppm SPECTRUM AMPL. 8 SWEEP TIME 5 min NUCLEUS______ SAMPLE: 3,5-Dinitroaniline OPERATOR KECK

LOCK POWER .002 mG FILTER .05 sec SWEEP WIDTH 10 ppm ZERO REF.______ DATE 4/8/78

DECOUPLE POS.______ ppm

DECOUPLING POWER______ mG RF POWER .04 mG END OF SWEEP______ ppm SAMPLE TEMP.______ °C SOLVENT: $CDCl_3$ w/1% (v/v) TMS SPECTRUM NO.______

FIGURE 172 NMR SPECTRUM OF 3,5-DINITROANILINE

varian instrument division palo alto, california

PART NO. 990089-00 PRINTED IN U.S.A.

008

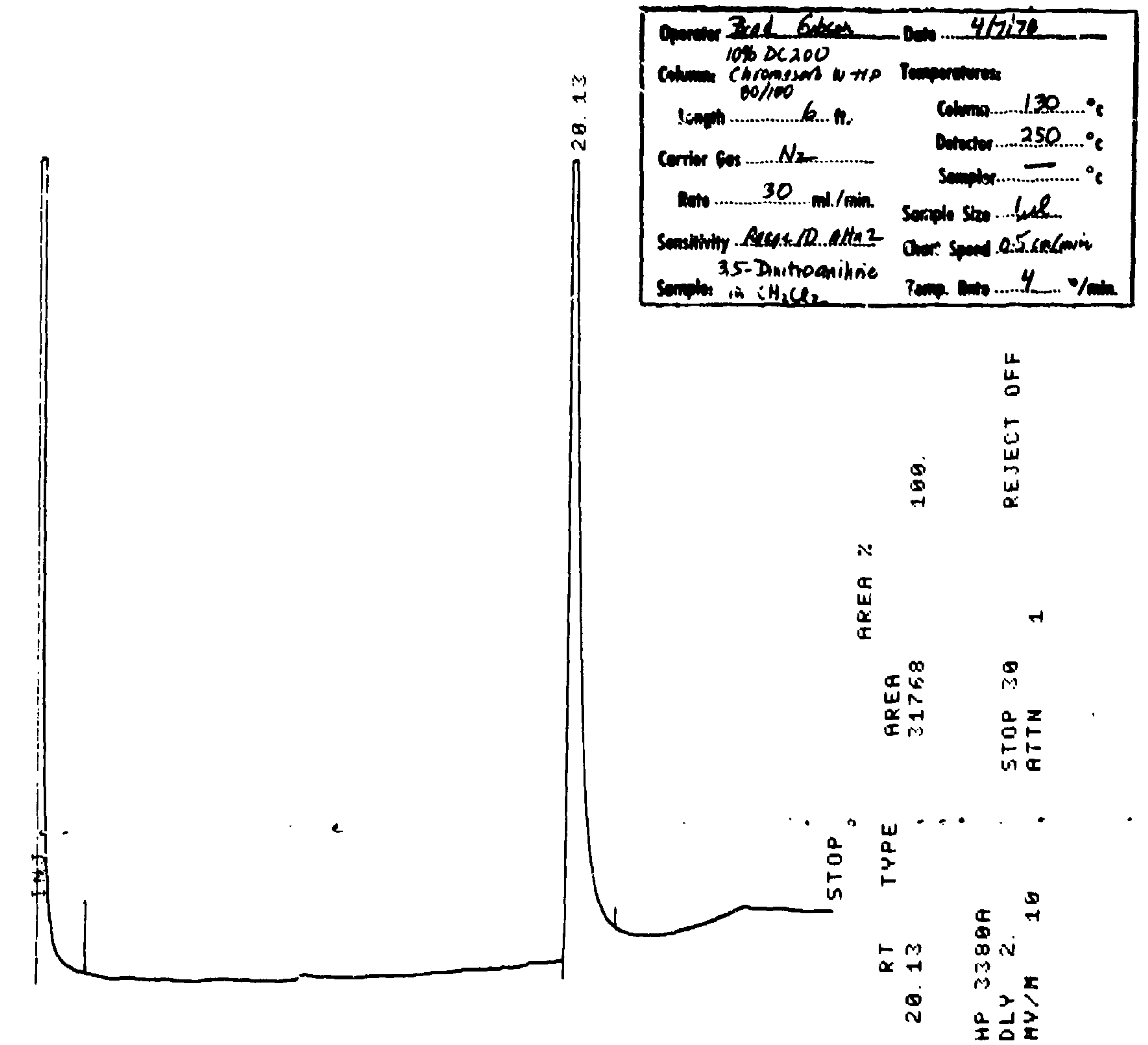
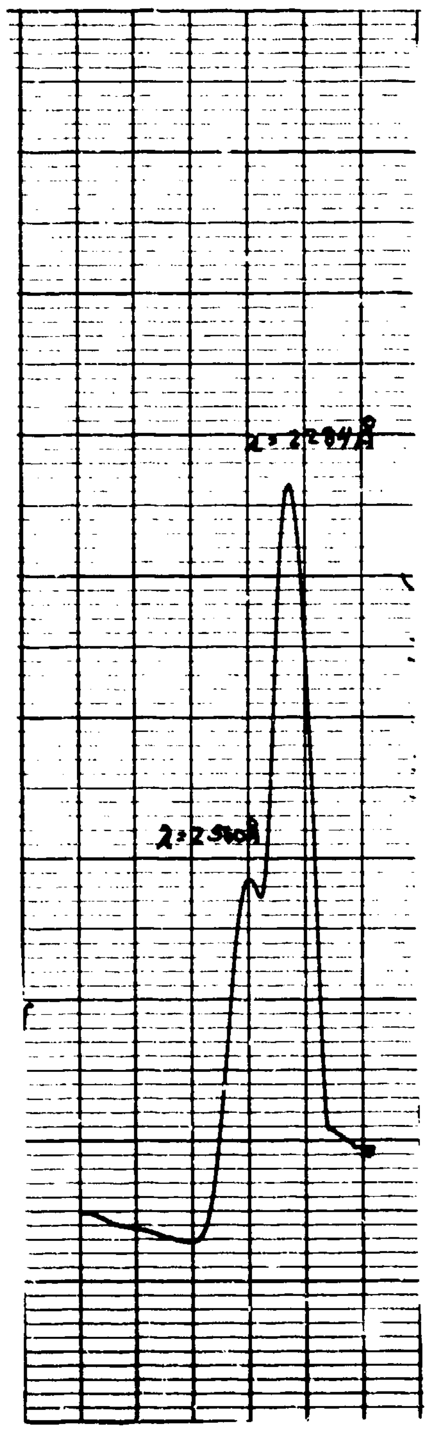


FIGURE 173 GC SPECTRUM OF 3,5-DINITROANILINE



3,5- Dinitroaniline

$c = 1.2 \times 10^{-4}$ m/l

$A_{2560} = 1.27$

$\varepsilon_{2560} = 10583$

$A_{2284} = 2.68$

$\varepsilon_{2284} = 22333$

FIGURE 174 UV SPECTRUM OF 3,5-DINITROANILINE

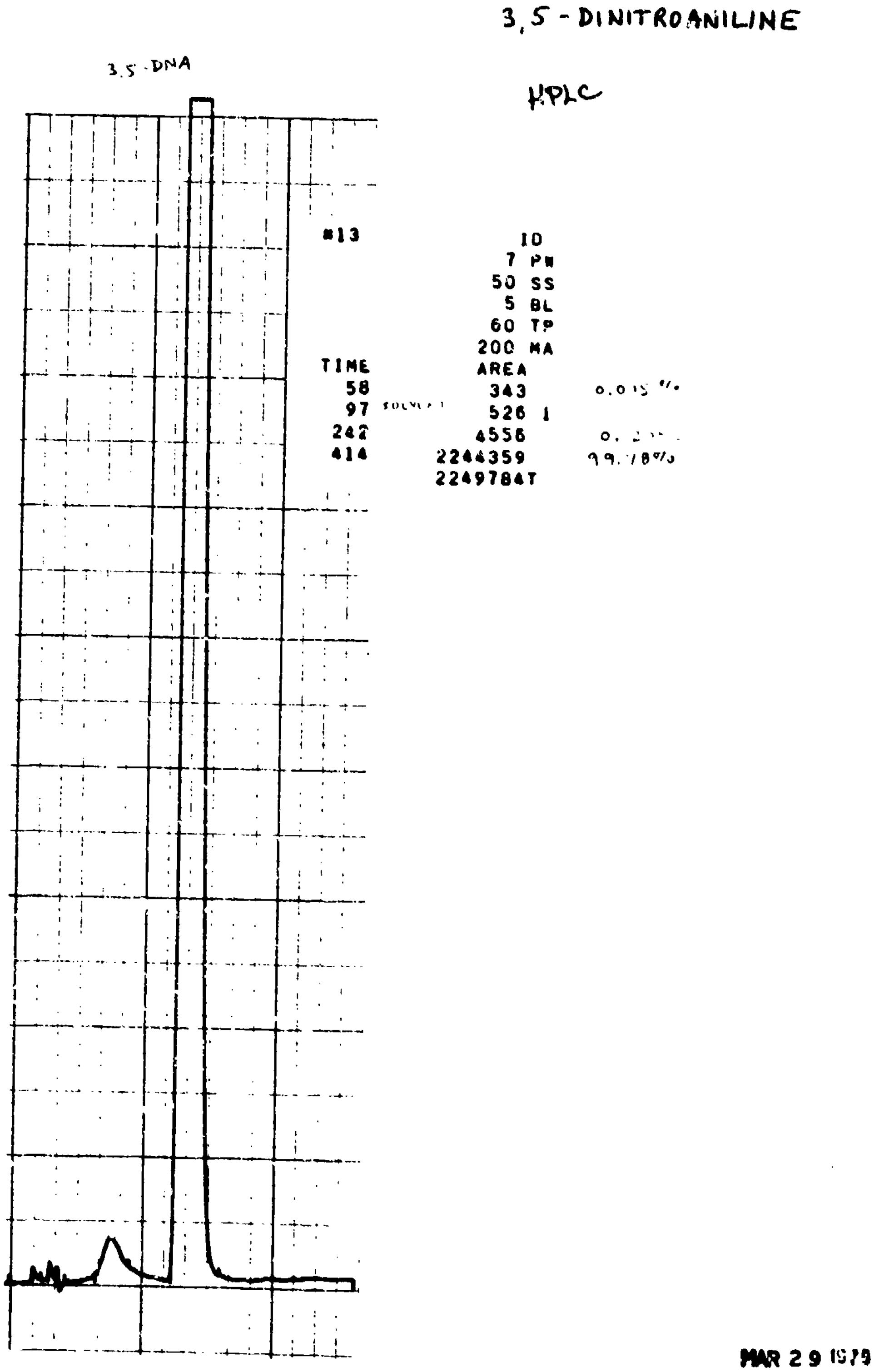


FIGURE 175 HPLC CHROMATOGRAM OF 3,5-DINITROANILINE

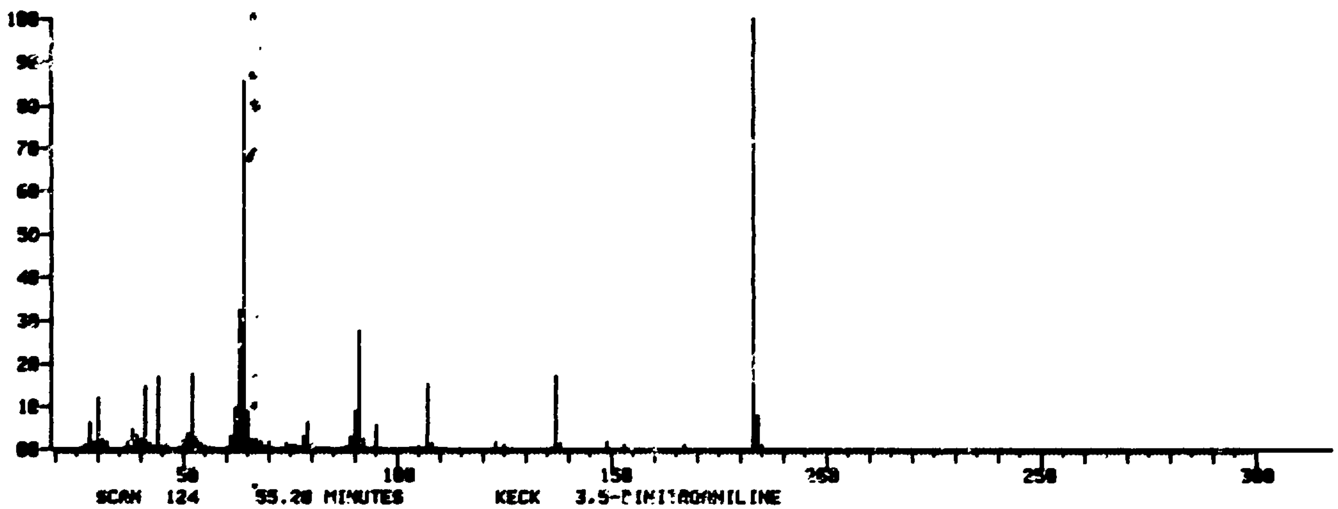
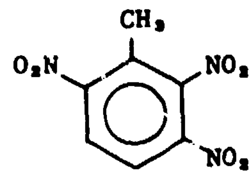
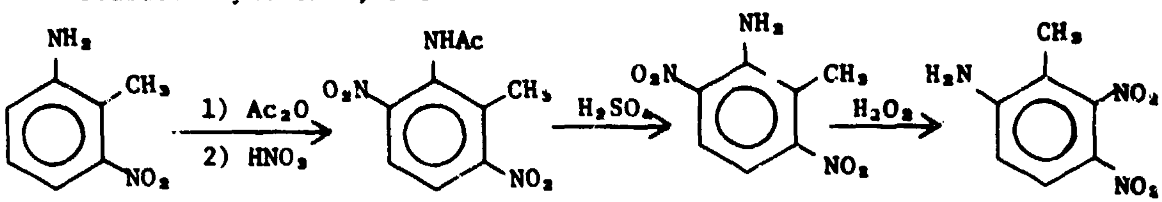


FIGURE 176 MASS SPECTRUM OF 3,5-DINITROANILINE

4.29 2,3,6-Trinitrotoluene
1-Methyl-2,3,6-trinitrobenzene
[18292-97-2]



Source: Synthesis, SRI



Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 3.23 (C-H, aromatic), 3.45 (C-H, methyl), 6.5, 7.45 (N=O), 7.1 (C=C, ring), 9.65, 13.95 (C-H), 11.38, 11.8 (C-H, aromatic NO_2), 7.75, 8.35, 8.75, 10.45, 12.03, 12.48, 12.95.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed and the number of protons each signal represents was determined from signal integrals:

δ 2.52 (singlet, 3H) CH_3
δ 8.10 (doublet, H, J_{a-b} = 3.0 cps) H_a
δ 8.25 (doublet, H, J_{b-a} = 3.0 cps) H_b.

Uv (Methanol)--λ_{max} = 207.9 nm, A - 0.326, ε = 19,880
λ_{max} = 252.0 nm, A = 0.138, ε = 8400
λ_{max} = 293.2 nm, A = 0.039, ε = 2380.

Purity (>99.3%)

Elemental Analysis--

Anal. for $C_7H_5N_3O_6$: Calcd: C, 37.01; H, 2.22; N, 18.5

Found: C, 36.88; H, 2.24; N, 17.5.*

High-Pressure Liquid Chromatography--One major component (representing 99.3% of the total peak areas) was observed by hplc. The following hplc conditions were used:

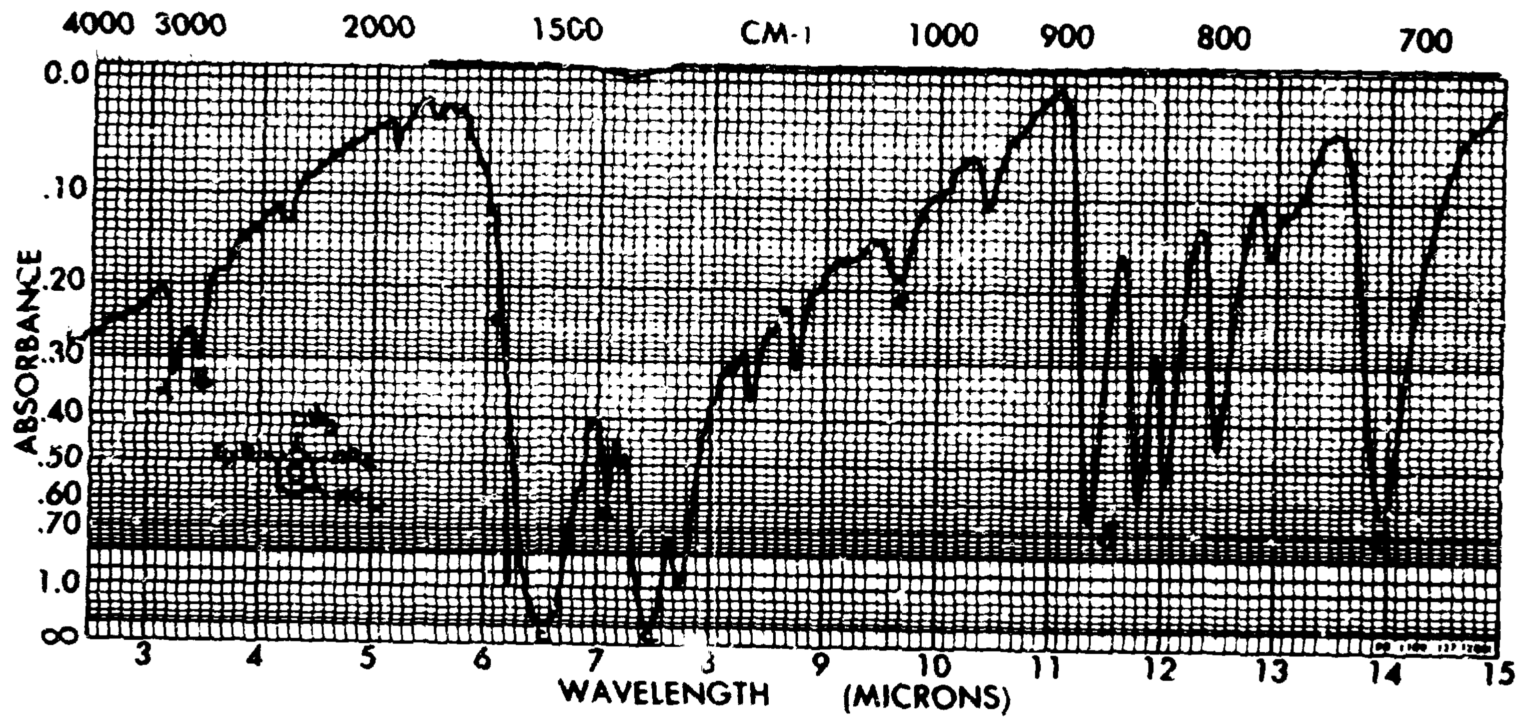
- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 nm
- Average retention time: 560 sec 2,3,6-trinitrotoluene 99.3%.

Gas Chromatography--One major component (representing at least 99.8% of the total peak areas) and one minor component were observed by gc under the following conditions:

- Column: 6' x 2 mm glass column packed with 10% DC200 on Chromasorb W-HP 80/100.
- Temperature: 130° (4 min) to 220° C at 4°/min.
- Flow rate: 30 ml/min N_2.
- Detection: Flame ionization.
- Retention time: 14.29 min 2,3,6-trinitrotoluene 99.8%+; 12.7 min impurity <0.2%.

---

* Some trinitro compounds tend to give low N results with the Perkin-Elmer analyzer.



SPECTRUM NO.	ORIGIN	LEGEND Ⓐ C-H aromatic Ⓑ C-H, CH_3 1. Ⓒ N=O Ⓓ C=C Ⓔ C-H 2. Ⓕ C-N, aromatic NO_2	REMARKS
SAMPLE 2,3,6-Trinitrotoluene	PURITY		
	PHASE	DATE 17 April 78	
	THICKNESS	OPERATOR KECK	

SPECTRUM NO.
SAMPLE

FIGURE 177 INFRARED SPECTRUM OF 2,3,6-TRINITROTOLUENE

006

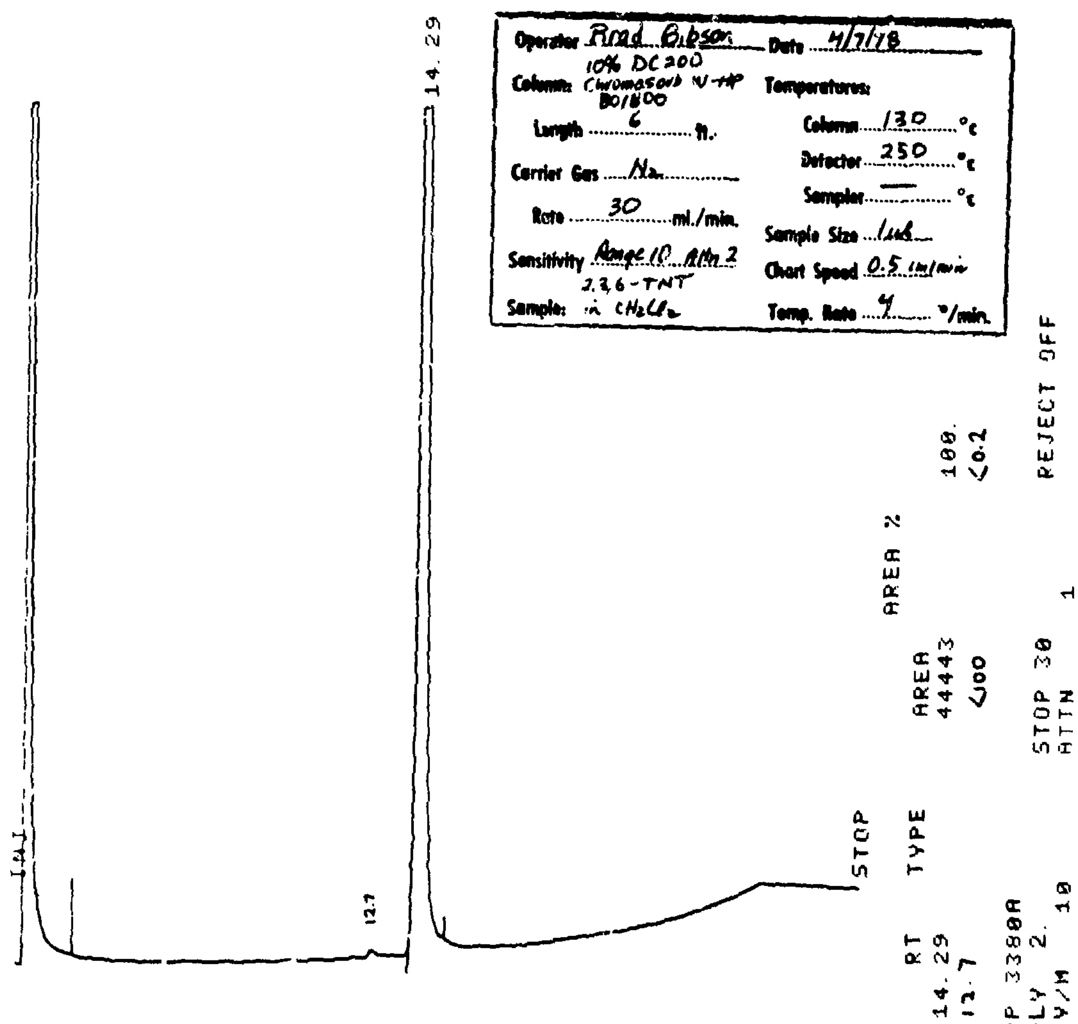
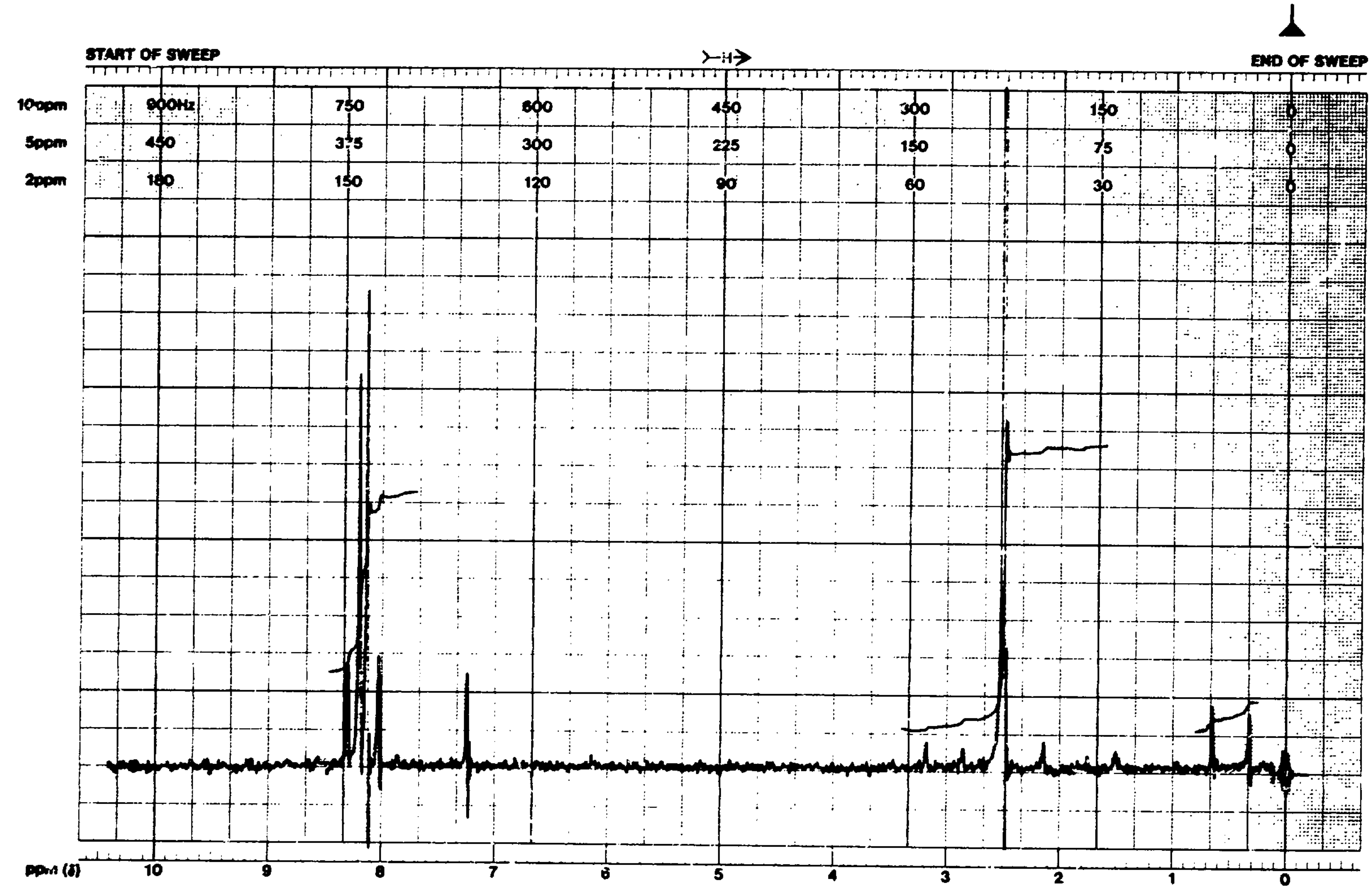


FIGURE 178 GC SPECTRUM OF 2,3,6-TRINITROTOLUENE

EM-390 90 MHz NMR SPECTROMETER



LOCK POS. ______ ppm
LOCK POWER .002 mG
DECOUPLE POS. ______ ppm
DECOUPLING POWER ______ mG

SPECTRUM AMPL. 5
FILTER .05 sec
RF POWER .04 mG

SWEEP TIME 5 min
SWEEP WIDTH 10 ppm
END OF SWEEP ______ ppm

NUCLEUS ______
ZERO REF. ______
SAMPLE TEMP. ______ °C

SAMPLE: 2,3,6-Trinitrotoluene
SOLVENT: CDCl$_3$ w/1% (v/v) TMS

OPERATOR Keck
DATE 4/8/78
SPECTRUM NO. ______

FIGURE 179 NMR SPECTRUM OF 2,3,6-TRINITROTOLUENE

2, 3, 6 - TRINITROTOLUENE

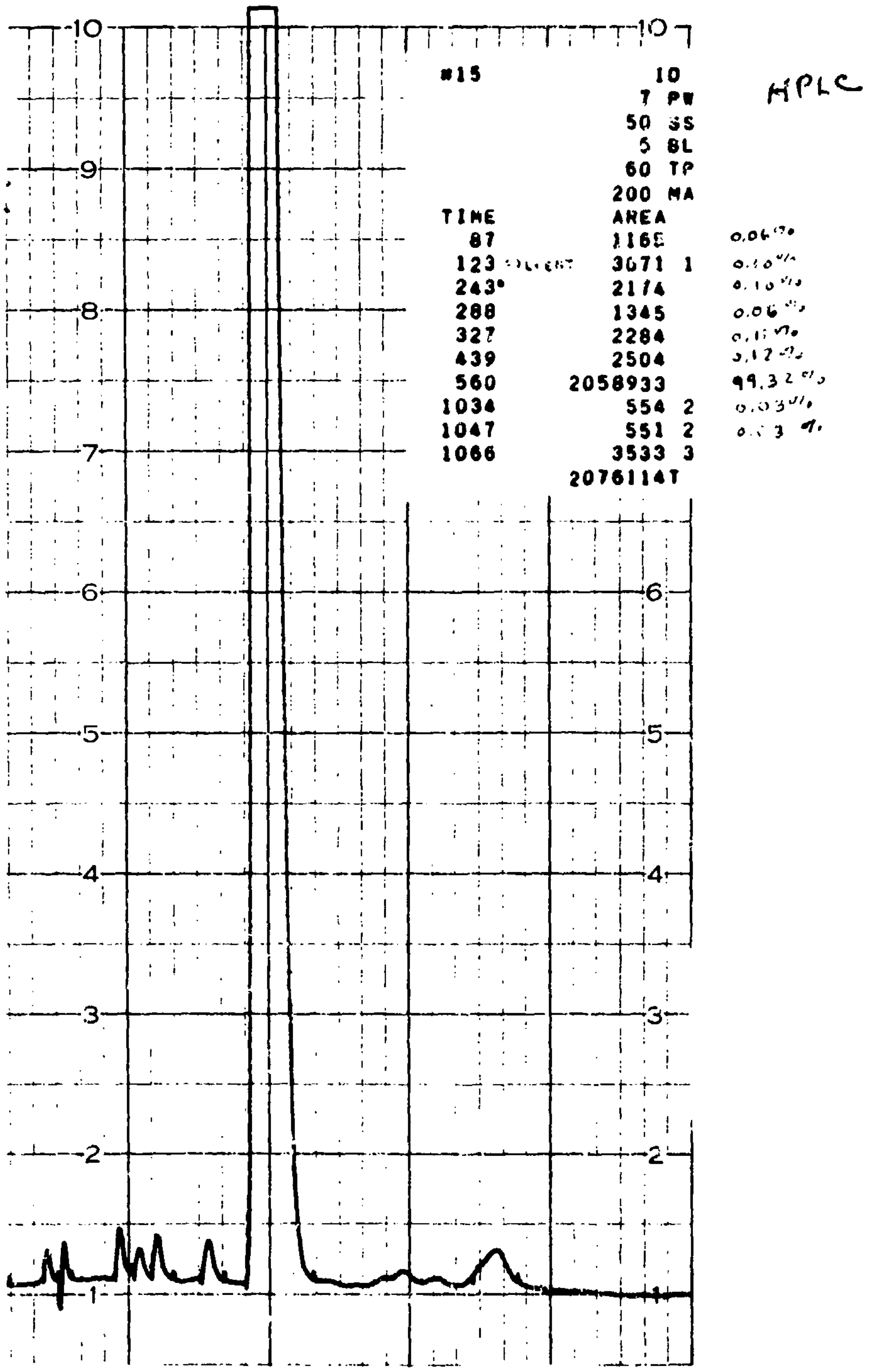


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FIGURE 180 HPLC CHROMATOGRAM OF 2,3,6-TRINITROTOLUENE

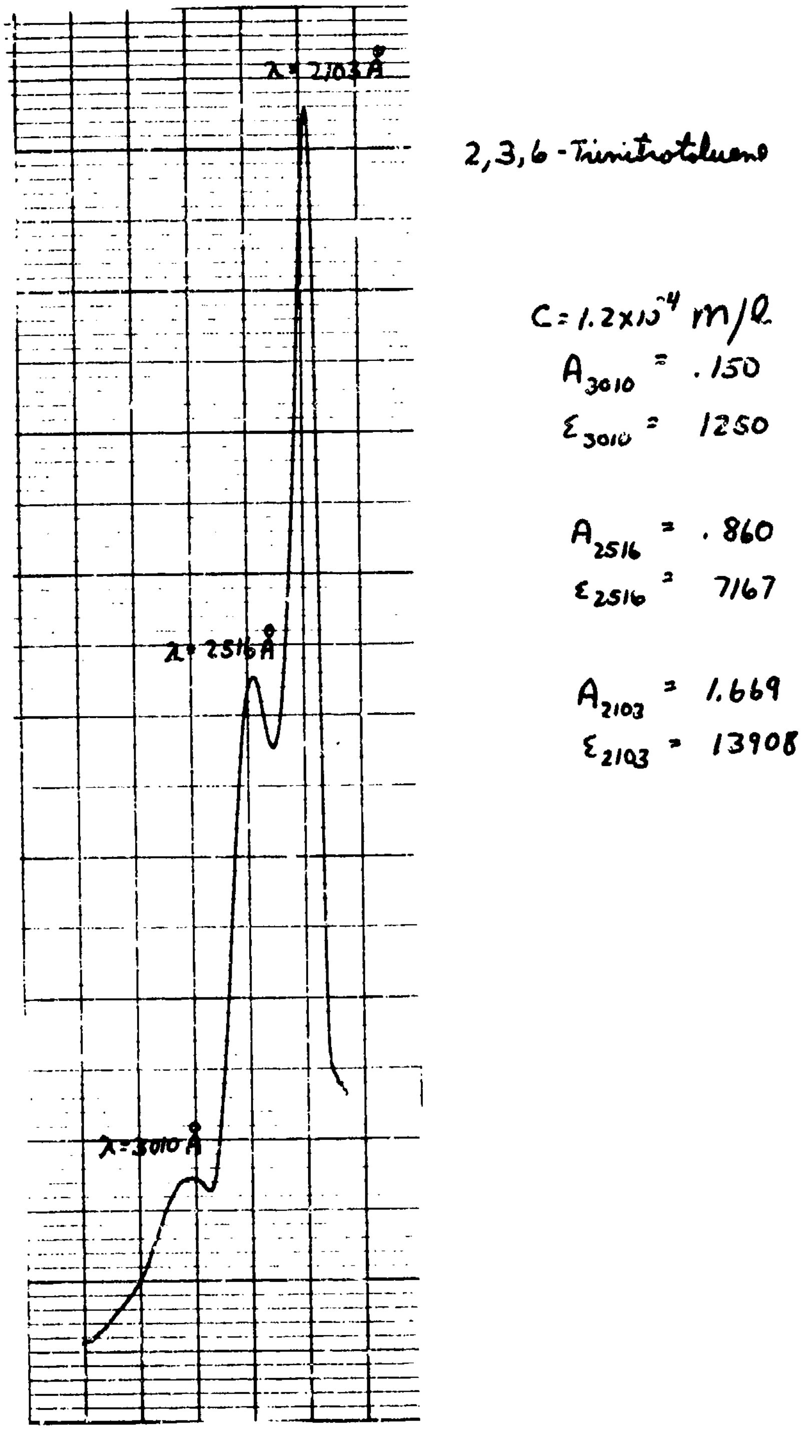


FIGURE 181 UV SPECTRUM OF 2,3,6-TRINITROTOLUENE

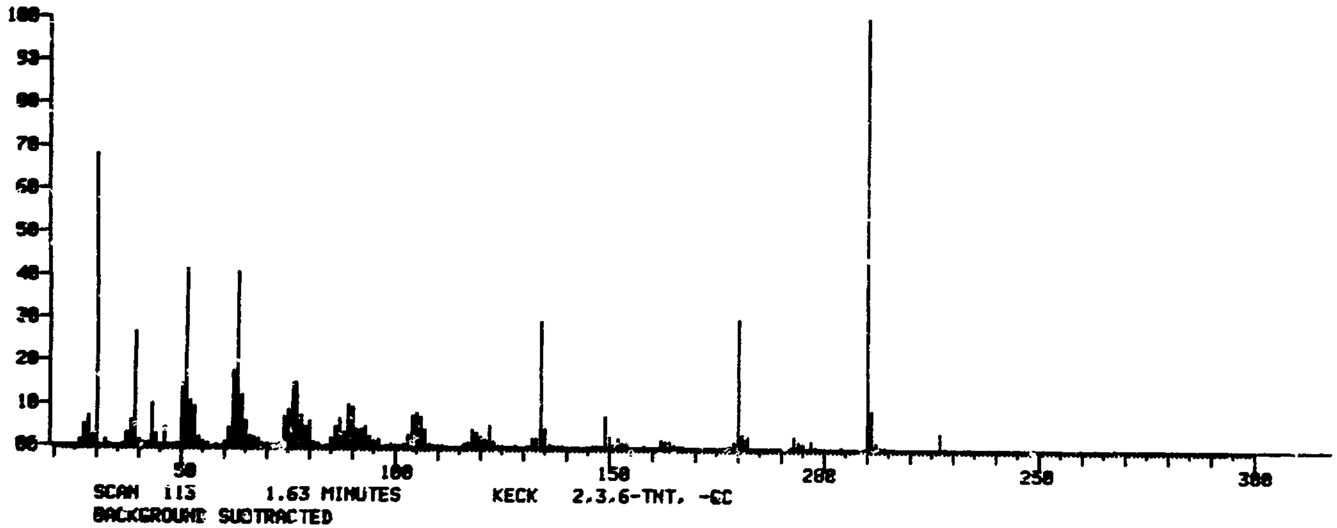
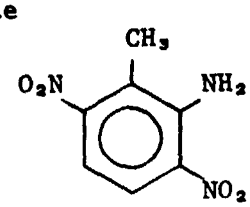
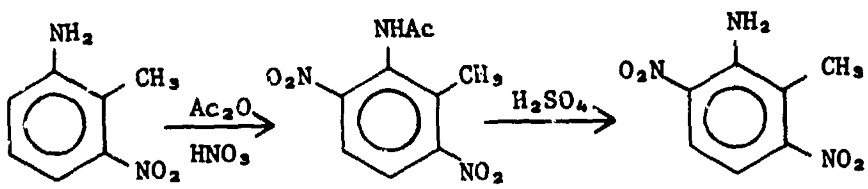


FIGURE 182 MASS SPECTRUM OF 2,3,6-TRINITROTOLUENE

4.30 2-Amino-3,6-Dinitrotoluene
2-Methyl-3,6-dinitrobenzenamine
[56207-39-7]



Source: Synthesis, SRI



Identity

Ir--The ir spectrum was consistent with the proposed structure. The following bands were observed: (KBr pellet) 2.90, 2.98, (N-H, 1° aromatic amines), 6.18, 7.0 (C=C, ring), 6.6, 7.45 (N=O), 7.95 (C-N, 1° aromatic amines), 12.19 (C-N, aromatic NO_2), 13.60 (C-N), 7.7, 8.45, 8.7, 11.55, 13.0 µm.

Nmr--The nmr spectrum was consistent with the proposed structure. The following chemical shifts were observed, and the number of protons each signal represents was determined from signal integrals:

δ 2.23 (singlet, 3H) CH_3
δ 6.40 (singlet, 2N) NH_2
δ 7.10 (doublet, H, J_{a-b} = 3.0 cps) H_a
δ 8.12 (doublet, H, J_{b-a} = 3.0 cps) H_b.

Uv (Methanol)--λ_{max} = 229.4 nm, A = 0.211, ε = 18,100
λ_{max} = 276.9 nm, A = 0.046, ε = 3950.

Elemental Analysis--

Anal. for $C_7H_7N_3O_4$: Calcd: C, 42.65; H, 3.58; N, 21.31

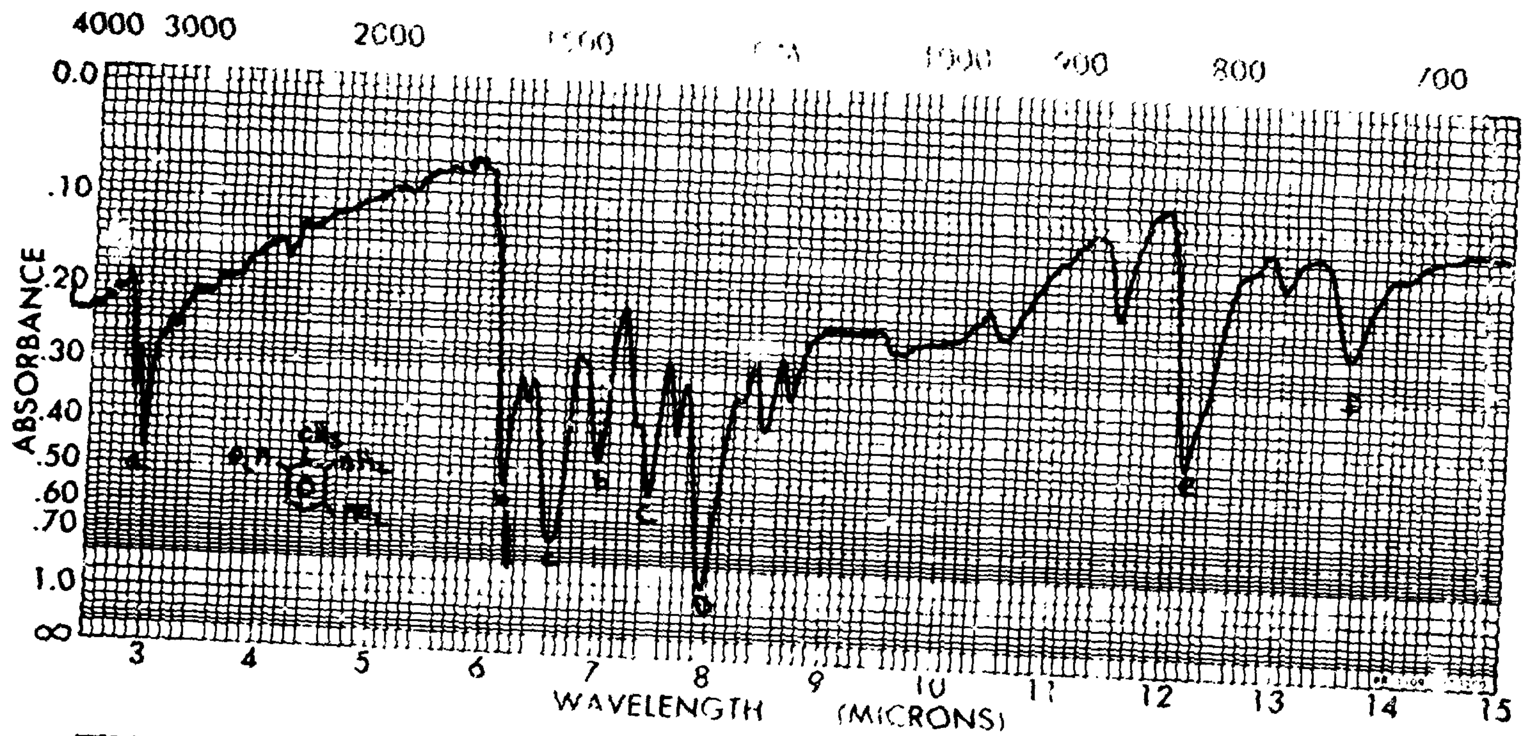
Found: C, 42.82; H, 3.67; N, 21.13.

High-Pressure Liquid Chromatography--One major component (representing 99.89% of total peak areas) and one minor component were observed by hplc. The following hplc conditions were used:

- Column: 4 mm ID x 30 cm μ Bondapak C_{18} (Waters Assoc.)
- Solvent: 50% H_2O/50% CH_3OH
- Flow rate: 2.0 ml/min
- Detection: uv at 254 nm
- Average retention time: 571 sec 2-amino-3,6-dinitrotoluene 99.89%; 283 sec impurity 0.11%.

Gas Chromatography--One major component (representing 100% of total peak areas) was observed by gc under the following conditions:

- Column: 6' x 2 mm glass packed with 10% DC 200 on Chromasorb W-HP 80/100.
- Temperature: 130° C (4 min) to 220° C at 4°/min.
- Flow rate: 30 ml/min.
- Detection: Flame ionization.
- Retention time: 17.21 min 2-amino-3,6-dinitrotoluene 100%.



SPECTRUM NO.

SAMPLE 2-Amino-3,6-Dinitrotoluene

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND
a n-H, 1° aromatic amine
b C=C
c N=O
d C-N, 1° aromatic amine
e C-N, aromatic NO_2
2 C-H

DATE 17 April 78

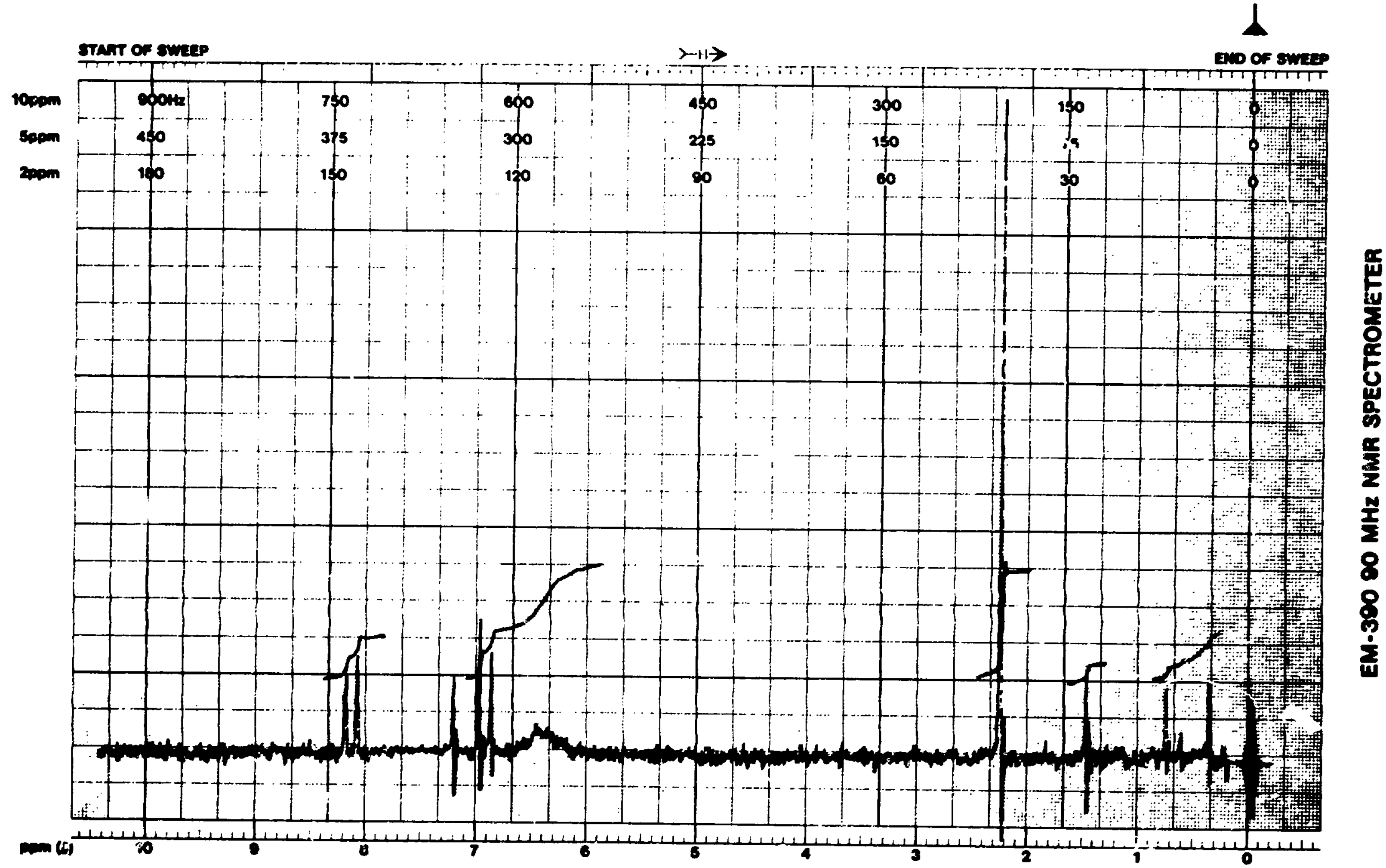
OPERATOR Keck

REMARKS

SPECTRUM NO.
SAMPLE

RECORDING CHARTS

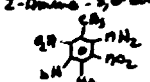
FIGURE 183 INFRARED SPECTRUM OF 2-AMINO-3,6-DINITROTOLUENE



LOCK POS.______ ppm   SPECTRUM AMPL. 7   SWEEP TIME 5 min   NUCLEUS______   SAMPLE: 2-Amino-3,6-dinitrotoluene   OPERATOR Keck

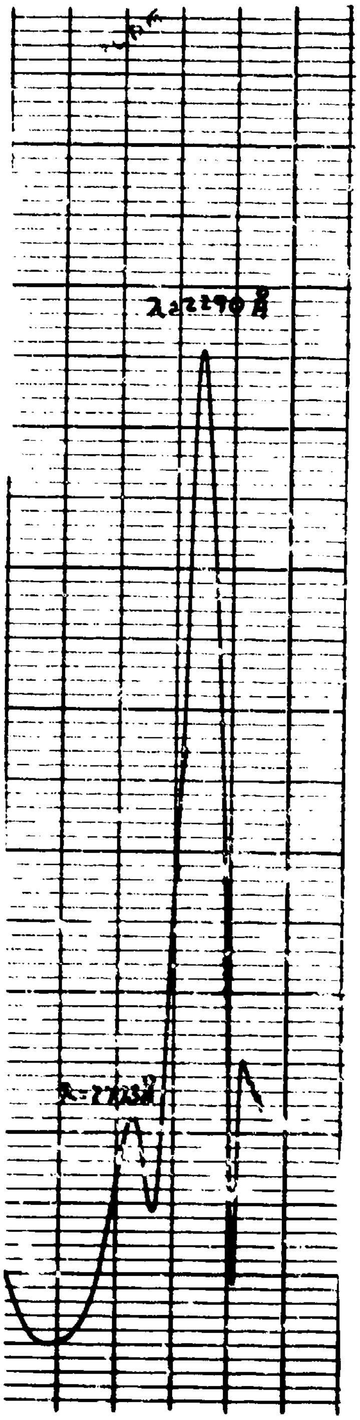
LOCK POWER .002 mG   FILTER .05 sec   SWEEP WIDTH 10 ppm   ZERO REF.______   DATE 4/8/78

DECOUPLE POS.______ ppm



DECOUPLING POWER______ mG   RF POWER .04 mG   END OF SWEEP______ ppm   SAMPLE TEMP.______ °C   SOLVENT: $CDCl_3$ w/1% (v/v) TMS   SPECTRUM NO.______

FIGURE 184 NMR SPECTRUM F 2-AMINO-3,6-DINITROTOLUENE



2-amino-3,6-Dinitrotoluene

$C = 6.0 \times 10^{-5}\ m/l$

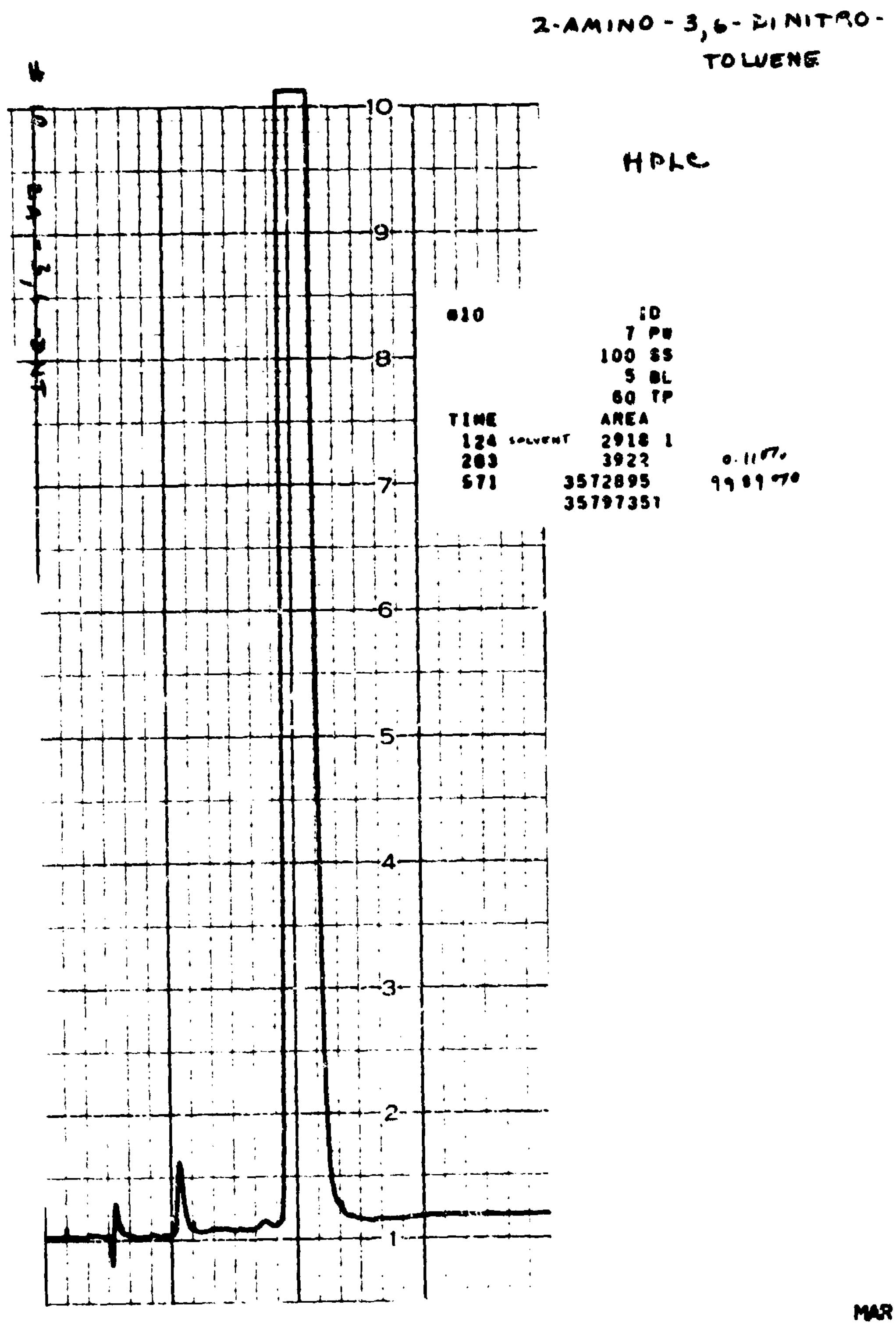
$A_{2773} = .112$

$\varepsilon_{2773} = 1867$

$A_{2290} = .658$

$\varepsilon_{2290} = 10967$

FIGURE 185 UV SPECTRUM OF 2-AMINO-3,6-DINITROTOLUENE



MAR 29 1978

FIGURE 186 HPLC CHROMATOGRAM OF 2-AMINO-3,6-DINITROTOLUENE

009

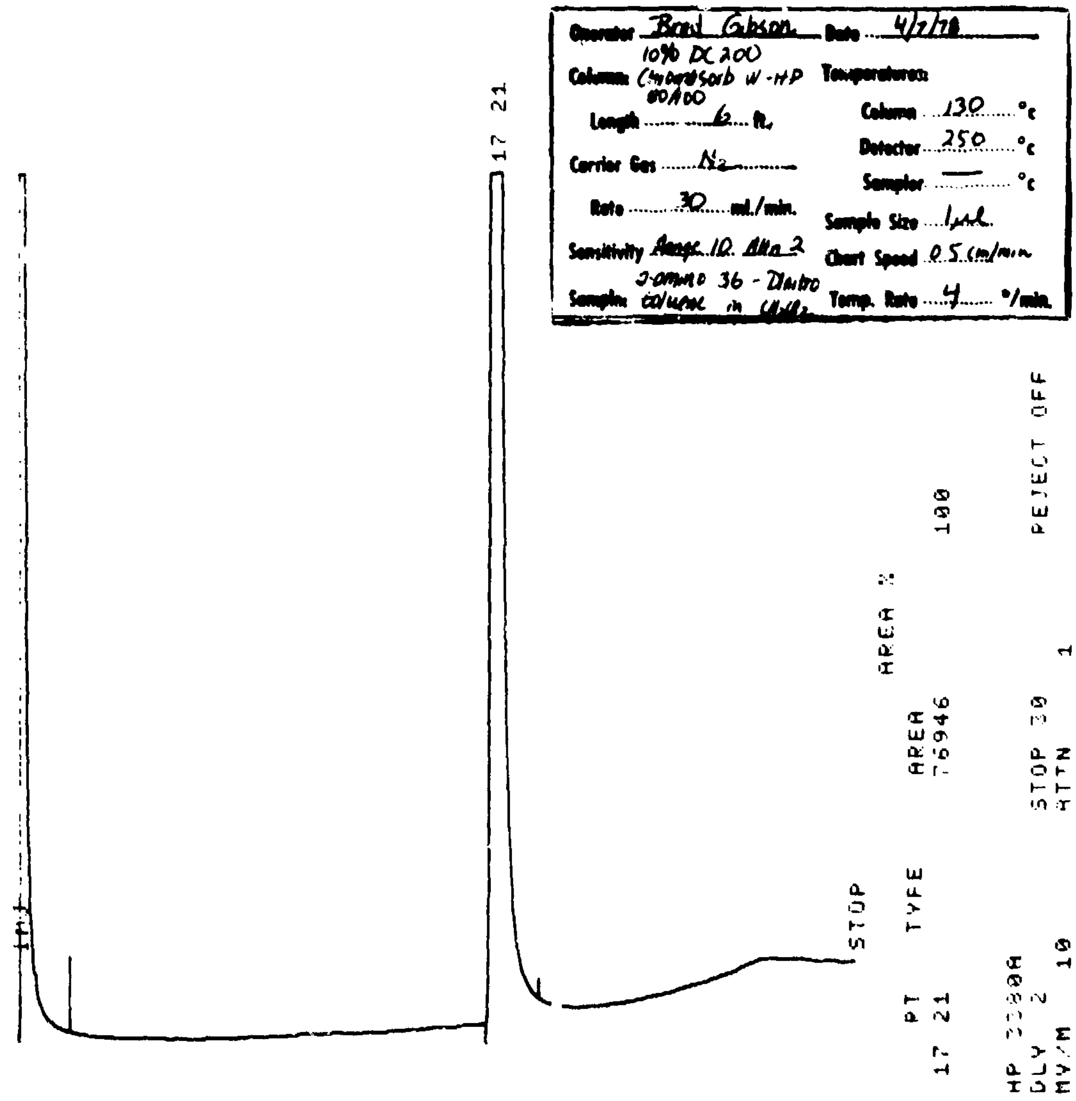


FIGURE 187 GC SPECTRUM OF 2-AMINO-3,6-DINITROTOLUENE

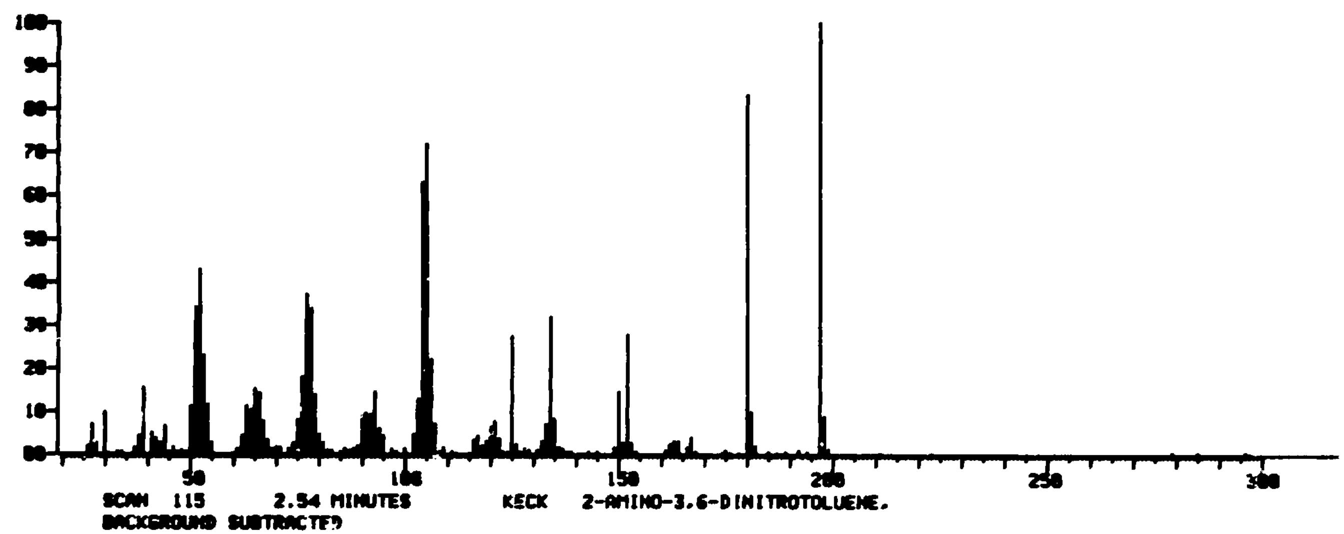


FIGURE 188 MASS SPECTRUM OF 2-AMINO-3,6-DINITROTOLUENE

5 ENVIRONMENTAL FATE ESTIMATES FOR CONDENSATE COMPONENTS

The introduction of condensate components into the environment through wastewater discharge creates concern not only about the environmental impact of the mixture and the individual components, but also about the potential transformation products resulting from environmental processes such as photolysis.

For determination of which compounds may be photolytically labile, the condensate mixture was photolyzed in the flow-through reactor as described in Section 3.4.2, and the individual components were monitored by gas chromatography. Exhibit B lists the compounds that were found to be photolytically reactive and those that were nonphotolytically reactive.

An evaluation of the structures of the compounds in Exhibit B indicates that one requirement for the occurrence of photolysis is that the molecule must have a nitro group positioned <u>ortho</u> to a methyl group. The only compound without this characteristic is 3-amino-2,4-dinitrotoluene; its nonphotolability can be explained by an intramolecular association of the nitro group with the amino function. This interaction inhibits the <u>ortho</u> nitro group from interaction with the methyl group.

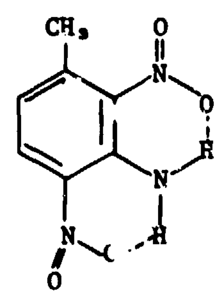


Exhibit B

PHOTOREACTIVITY OF CONDENSATE COMPONENTS

Photoreactive	Nonphotoreactive
2,6-Dinitrotoluene	1,3-Dinitrobenzene
2,5-Dinitrotoluene	3,5-Dinitrotoluene
3-Amino-2,6-dinitrotoluene	3,4-Dinitrotoluene
4-Amino-2,6-dinitrotoluene	3-Amino-2,4-dinitrotoluene
2,3-Dinitrotoluene	4-Nitrotoluene
2,4-Dinitrotoluene	3-Amino-4-nitrotoluene
1,5-Dimethyl-2,4-dinitrobenzene	Toluene
2-Nitrotoluene	5-Methyl-2-nitrophenol
1-Amino-6-nitrotoluene	4-Nitrobenzonitrile
2,4,6-Trinitrotoluene	3-Nitrobenzonitrile
5-Amino-2,4-dinitrotoluene	2-Amino-4-nitrotoluene
4-Amino-3,5-dinitrotoluene	1,3,5-Trinitrobenzene
2-Amino-3,6-dinitrotoluene	3,5-Dinitroaniline
2,3,6-Trinitrotoluene	
2-Amino-4,6-dinitrotoluene	
3-Methyl-2-nitrophenol	

To evaluate the effects of photolysis in sunlight as compared with the laboratory photolysis results, we performed a rooftop study similar to the one described in Section 3.4.2. This study revealed that the concentrations of many of the components that had not been determined to be photoreactive in laboratory studies did decrease as a function of time in sunlight. We postulated that volatility may affect these chemicals in aqueous systems.

To test this hypothesis, we used a 4400-ml aqueous solution containing the condensate components listed in Table 13, divided it in half, and poured it into two identical glass containers. Each container was lined with paper so that photolysis could occur only near the surface of the solution. One container was placed in the sunlight, and the other was placed approximately 5 feet away in an area that was continuously shaded. Each solution was stirred with a magnetic stir bar at equal rates, and samples were removed periodically for capillary gc analysis and measurement of water loss. Water loss from each solution averaged 250 ml/day for the sun solution and 200 ml/day for the shade solution. These volumes were added to each solution before sampling for gc analysis.

Table 14 presents the results of these experiments, which indicate that both photolysis and volatility can be important factors in determining the fate of condensate components in water. The condensate components can be grouped into three categories: Group 1, in which volatility is the only factor affecting compound loss; Group 2, in which volatility and photolysis are both important; and Group 3, in which photolysis is the predominant factor.

The chemicals in Group 1 are 1,3-dinitrobenzene, 3,5-dinitrotoluene, 3,4-dinitrotoluene, 3-amino-2,4-dinitrotoluene, 2-nitrotoluene, and 4-nitrotoluene. Plots of the concentration of these compounds against time are linear. The slopes of these lines differ by 1.2, which is the ratio of the water loss between sun and shade.

Table 13

CONCENTRATIONS OF CONDENSATE COMPONENTS
USED IN SUN-SHADE EXPERIMENT

Component	Concentration (mg/liter)
2-Nitrotoluene	0.08
4-Nitrotoluene	0.32
2,6-Dinitrotoluene	14.5
1,3-Dinitrobenzene	11.3
2,5-Dinitrotoluene	0.87
2,4-Dinitrotoluene	37.0
2,3-Dinitrotoluene	1.1
3,5-Dinitrotoluene	0.91
3,4-Dinitrotoluene	1.0
1,5-Dimethyl-2,4-dinitrobenzene	0.70
3-Amino-2,4-dinitrotoluene	3.35
4-Amino-3,5-dinitrotoluene	0.25
3-Amino-2,6-dinitrotoluene	3.1
4-Amino-2,6-dinitrotoluene	1.2
5-Amino-2,4-dinitrotoluene	1.1

Table 14

CONCENTRATIONS OF CONDENSATE COMPONENTS DURING SUN-SHADE EXPERIMENT (Milligrams per Liter)

Time (hr)	o-NT	p-NT	1,3-DNB	2,6-DNT	2,5-DNT	2,4-DNT	2,3-DNT	3,5-DNT	3,4-DNT	DNX	197 A	197 E	197 B	197 C	197 D	
To	.077	0.032	11.4	14.5	0.87	29.2	1.05	0.91	1.00	0.70	3.35	0.25	3.12	1.21	1.10	Sun
24	+	0.06	11.0	9.3	0.48	26.6	0.86	0.89	0.96	0.60	2.97	*	1.53	0.80	1.10	
48	-	-	10.4	3.0	0.22	23.2	0.83	0.80	0.90	0.50	*	*	0.59	0.35	*	
72	-	-	9.7	0.5	0.07	19.2	0.70	0.74	0.84	0.37	2.87	0.18	0.16	0.20	1.03	
168	-	-	7.8	-	-	8.6	0.32	0.54	0.64	0.08	2.27	0.14	-	-	*	
240	-	-	6.4	-	-	4.2	0.09	0.39	0.45	-	1.64	0.08	-	-	0.68	
312	-	-	5.1	-	-	1.9	0.01	0.27	0.36	-	1.41	0.08	-	-	0.61	
408	-		3.2	-	0	0.6	-	0.16	0.19	-	1.04	0.05	-	-	0.52	
24	0.037	.	10.1	12.1	0.77	26.1	0.93	0.86	0.85	0.63	3.17	0.23	3.00	1.30	1.27	Shade
48	-	-	10.2	10.6	0.73	25.2	0.86	0.79	0.90	0.58	3.20	0.23	2.95	1.23	1.14	
72	-	-	10.0	9.5	0.66	24.4	0.85	0.82	0.85	0.56	3.21	0.23	2.94	1.17	1.08	
168	-	-	8.4	5.4	0.34	19.5	0.54	0.62	0.64	0.42	2.70	0.21	2.62	1.16	1.12	
240	-	-	7.2	3.1	0.15	15.7	0.37	0.54	0.55	0.30	2.44	0.18	2.22	1.12	1.06	
312	-	-	6.2	1.6	0.10	12.5	0.10	0.44	0.55	0.22	2.30	*	2.18	*	*	
408	-	-	4.6	0.51	-	8.1	0.07	0.26	0.36	0.11	1.77	0.15	1.66	0.90	1.02	

+Observed, not detected by integrator.
-Not detected.
*Erroneous integration.
DNX, 1,5-Dimethyl-2,4-dinitrotoluene

197A, 3-Amino-2,4-dinitrotoluene.
197E, 4-Amino-3,5-dinitrotoluene.
197B, 3-Amino-2,6-dinitrotoluene.
197C, 4-Amino-2,6-dinitrotoluene.
197D, 5-Amino-2,4-dinitrotoluene.

The Group 2 chemicals are 2,3-dinitrotoluene, 2,4-dinitrotoluene, 1,5-dimethyl-2,4-dinitrobenzene, 4-amino-3,5-dinitrotoluene, and 5-amino-2,4-dinitrotoluene. In this group, both photolysis and volatility are important, but the effect is least pronounced in the aminodinitrotoluene compounds. The comparative losses for these compounds indicate that the two processes are competitive.

The Group 3 chemicals are 2,6-dinitrotoluene, 2,5-dinitrotoluene, 3-amino-2,6-dinitrotoluene, and 4-amino-2,6-dinitrotoluene. In this group, the effect of photolysis is dramatic and indicates that volatilization plays a limited rose in describing the fate of these compounds.

We performed a similar study in the laboratory to confirm condensate component losses due to volatilization. A solution containing condensate components was placed in a darkened hood under conditions similar to those used in the rooftop study. Component losses were monitored periodically and are presented in Table 15. The component losses were similar to those observed in the shade rooftop experiment. A comparison of the percentage of loss at 192 hours in this study and at 240 hours in the shade rooftop study (bottom of Table 15) shows relative component losses, indicating that the same factor (volatilization) operates in both cases. These results indicate the significance of volatilization in describing the fate of condensate components in fresh water.

To obtain an indication of the contribution and magnitude of volatility and photolysis in describing the fate of condensate components, pseudo first-order rate constants were determined for each process using the data in Table 14. The rate constant for volatilization was generated from the shade experiment using the equation

$$\frac{ds}{dt} = k_v^s \; [S] \quad , \qquad (8)$$

Table 15

COMPARATIVE VOLATILITY STUDIES OF CONDENSATE COMPONENTS* UNDER OUTDOOR SHADE AND CONTROLLED LABORATORY CONDITIONS

Time (hr)	Concentration Found														
	o-NT	p-NT	m-DNB	2,6-DNT	2,5-DNT	2,4-DNT	2,3-DNT	3,5-DNT	3,4-DNT	DNX	197A	197E	197B	197C	197D
Laboratory															
0	0.10	0.35	12.0	18.3	0.96	43.7	1.3	1.1	1.1	1.0	5.2	0.31	4.1	1.4	1.2
48	--	--	10.8	12.7	0.73	36.7	1.14	0.94	0.93	0.79	4.80	0.31	3.92	1.34	1.12
96	--	--	9.84	8.62	0.57	31.8	0.77	0.82	0.87	0.64	4.72	0.30	3.92	1.34	1.14
144	--	--	8.33	5.11	0.36	24.3	0.54	0.69	0.75	0.49	4.30	0.30	3.87	1.34	1.20
192	--	--	7.04	2.96	0.20	18.5	0.48	0.56	0.70	0.39	4.16	0.30	4.00	1.36	1.20
Loss (%)	100	100	41.3	83.8	77.5	57.6	63.2	49.0	35.1	61.4	20	3	0	0	0
Shade															
0	0.77	0.032	11.4	14.5	.87	29.2	1.05	0.91	1.00	0.70	3.35	0.25	3.12	1.21	1.10
Loss at 240 hr (%)	100	100	37.9	88.7	82.8	46.3	64.8	40.7	45.0	51.2	27.2	28.0	28.9	7.4	3.7

* See footnote to Table 14 for full names of compounds.

where k_v^s is the volatilization rate constant for substrate S. A pseudo first-order rate constant was also generated from the sun experiment using a similar equation,

$$\frac{-ds}{dt} = k_{v+p}^s \, [S] \quad , \tag{9}$$

where the rate constant k_{v+p}^s is related to both the volatilization and photolysis processes by

$$k_{v+p}^s = 1.2k_v^s + k_p^s \quad . \tag{10}$$

The factor 1.2 was used to reflect the difference in water loss between the sun and shade experiments. Since k_{v+p}^s and k_v^s were measured, k_p^s could be calculated.

Using this approach, the k_p^s and k_v^s values were calculated and are listed in Table 16 for 15 condensate components. These rate constants should not be used to calculate environmental half-lives; they serve only to give a relative magnitude of the processes between compounds.

By normalizing the rate constants, we calculated the percentage of contribution of photolysis and volatility to the loss of condensate compounds from water; Table 17 presents these data.

The rate constants were combined and are listed in decreasing order in Table 18. By listing the compounds in this manner, some order of persistence can be established for this condensate mixture. Thus, 3,4-dinitrotoluene, 4-amino-3,5-dinitrotoluene, 3-amino-2,4-dinitrotoluene, 1,3-dinitrobenzene, 3,5-dinitrotoluene, and 5-amino-2,4-dinitrotoluene would be expected to persist the longest in the environment, excluding such fates as sediment adsorption and biotransformation.

Table 16

RELATIVE RATES OF LOSS OF CONDENSATE COMPONENTS
DUE TO VOLATILITY AND PHOTOLYSIS

Component	$k \times 10^{-2}$ (ppm/hr)
Volatilization	
4-Nitrotoluene	49.9
2-Nitrotoluene	25.9
2,6-Dinitrotoluene	5.64
2,5-Dinitrotoluene	4.01
2,3-Dinitrotoluene	3.47
1,5-Dimethyl-2,4-dinitrobenzene	2.81
3,4-Dinitrotoluene	2.57
2,4-Dinitrotoluene	2.37
3,5-Dinitrotoluene	2.28
1,3-Dinitrobenzene	1.88
3-Amino-2,4-dinitrotoluene	1.20
3-Amino-2,6-dinitrotoluene	1.15
4-Amino-3,5-dinitrotoluene	1.15
4-Amino-2,6-dinitrotoluene	0.30
5-Amino-2,4-dinitrotoluene	0.00
Photolysis	
2-Nitrotoluene	19.00
3-Amino-2,6-dinitrotoluene	14.58
2,5-Dinitrotoluene	10.01
2,6-Dinitrotoluene	7.53
4-Amino-2,6-dinitrotoluene	5.95
1,5-Dimethyl-2,4-dinitrobenzene	2.29
2,4-Dinitrotoluene	1.83
5-Amino-2,4-dinitrotoluene	2.10
2,3-Dinitrotoluene	0.63
1,3-Dinitrobenzene	0
3,5-Dinitrotoluene	0
3,4-Dinitrotoluene	0
3-Amino-2,4-dinitrotoluene	0
4-Amino-3,5-dinitrotoluene	0
4-Nitrotoluene	0

Table 17

THE PERCENTAGE OF CONTRIBUTION OF PHOTOLYSIS AND VOLATILITY TO THE LOSS OF CONDENSATE COMPONENTS FROM WATER

Component	Percentage of Loss Due To:	
	Photolysis	Volatility
1,3-Dinitrobenzene	0	100
2,6-Dinitrotoluene	57.2	42.8
2,4-Dinitrotoluene	13.5	56.5
2,5-Dinitrotoluene	68.6	31.4
2,3-Dinitrotoluene	16	84
3,5-Dinitrotoluene	0	100
3,4-Dinitrotoluene	0	100
1,5-Dimethyl-2,4-dinitrobenzene	44.9	55.1
3-Amino-2,4-dinitrotoluane	0	100
3-Amino-2,6-dinitrotoluene	92.7	7.3
4-Amino-2,6-dinitrotoluene	95.2	4.8
2-Nitrotoluene	37.7	62.3
4-Nitrotoluene	0	100
5-Amino-2,4-dinitrotoluene	100	0
4-Amino-3,5-dinitrotoluene	0	100

Table 18

RELATIVE RATES OF LOSS OF CONDENSATE COMPONENTS FROM THE ENVIRONMENT AS A FUNCTION OF PHOTOLYSIS AND VOLATILITY

Compound	$k \times 10^{-2}$ (ppm/hr)
4-Nitrotoluene	49.6
2-Nitrotoluene	44.9
3-Amino-2,6-dinitrotoluene	15.74
2,5-Dinitrotoluene	14.02
2,6-Dinitrotoluene	13.17
4-Amino-2,6-dinitrotoluene	6.25
1,5-Dimethyl-2,4-dinitrobenzene	5.10
2,4-Dinitrotoluene	4.20
2,3-Dinitrotoluene	4.12
3,4-Dinitrotoluene	2.57
3,5-Dinitrotoluene	2.28
5-Amino-2,4-dinitrotoluene	2.10
1,3-Dinitrobenzene	1.88
3-Amino-2,4-dinitrotoluene	1.20
4-Amino-3,5-dinitrotoluene	1.15

To ascertain whether or not sediment adsorption and bioaccummulation may be significant factors in describing the environmental fate of condensate components, the octanol/water partition coefficients were calculated by computer according to the method of Leo et al[8] and are listed in Table 19. For some compounds, literature references could be obtained and are included in the table. The partition coefficients are closely related to each other, which is expected because of the similarity of the structures of the components. These values may be related to sediment adsorption, especially for sediments high in organic matter. However, caution should be used in ascribing any correlations with these compounds that have ionizable groups (such as the phenols and amines) since the adsorption of these compounds will depend on the cation exchange capacity of the sediment.

From the octanol/water partition coefficients, the log of the bioconcentration factor (BCF) was calculated for condensate components according to the method of Branson et al[9]. Table 20 presents these data. The bioconcentration factors range from 2.18 to 52.50. Bioconcentration of the condensate components in fish should not be significant according to the U.S. Army Medical Bioengineering Research and Development Laboratory aquatic technical advisors who believe that 1000 is a minimum value for the BCF before bioaccummulation is significant.

This preliminary estimate of environmental fates for condensate compounds indicates that volatilization and photolysis can play major roles in the removal or transformation of selected components in an aquatic system and that sediment adsorption and bioaccummulation may play only minor roles. The effects of biotransformation have not been considered in this study and we recommend that this fate be investigated, especially with respect to those compounds that show indications of environmental persistence.

Table 19

OCTANOL/WATER PARTITION VALUES (LOG P)
DETERMINED FOR CONDENSATE COMPONENTS

Compound	log P	Ref
2,4-Dinitrotoluene	2.28	1
2,6-Dinitrotoluene	2.285	6
1,3-Dinitrobenzene	1.62	6
3-Amino-2,4-dinitrotoluene	1.06	6
3-Amino-2,6-dinitrotoluene	1.06	6
5-Amino-2,4-dinitrotoluene	1.06	6
3,5-Dinitrotoluene	2.285	6
3,4-Dinitrotoluene	2.285	6
4-Amino-2,6-dinitrotoluene	1.06	6
1,5-Dimethyl-2,4-dinitrobenzene	2.95	6
2,3-Dinitrotoluene	2.285	6
2,5-Dinitrotoluene	2.285	6
2,4,6-Trinitrotoluene	2.03	6
4-Amino-3,5-dinitrotoluene	1.06	6
Toluene	2.69	2
	2.73	3
	2.11	4
	2.80	5
4-Nitrotoluene	2.37, 2.42	2, 5
2,4-Dinitro-5-methylphenol	1.62	6
2-Amino-6-nitrotoluene	1.315	6
3-Amino-4-nitrotoluene	1.315	6
2-Nitrotoluene	2.30	5
2-Amino-3,6-dinitrotoluene	1.06	6
2,3,6-Trinitrotoluene	2.03	6
2-Amino-4,6-dinitrotoluene	1.06	6
5-Methyl-2-nitrophenol	1.875	6
2-Amino-4-nitrotoluene	1.315	6
3-Methyl-2-nitrophenol	1.875	6
1,3,5-Trinitrobenzene	1.365	6
3,5-Dinitroaniline	0.395	6
3-Nitrobenzonitrile	1.17	2
4-Nitrobenzonitrile	1.19, 1.31	2, 6

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Table 20

CALCULATED LOG BCF VALUES FOR CONDENSATE WATER COMPONENTS

Compound	Log P	Log BCF*	BCF
3,5-Dinitrotoluene	0.395	0.338	2.18
3-Amino-2,4-dinitrotoluene	1.06	0.698	
3-Amino-2,6-dinitrotoluene	1.06	0.698	
5-Amino-2,4-dinitrotoluene	1.06	0.698	
4-Amino-2,6-dinitrotoluene	1.06	0.698	
4-Amino-3,5-dinitrotoluene	1.06	0.698	
2-Amino-3,6-dinitrotoluene	1.06	0.698	
2-Amino-4,6-dinitrotoluene	1.06	0.698	
3-Nitrobenzonitrile	1.17	0.758	
4-Nitrobenzonitrile	1.19	0.769	
2-Amino-6-nitrotoluene	1.32	0.839	
3-Amino-4-nitrotoluene	1.32	0.839	
2-Amino-4-nitrotoluene	1.32	0.839	
1,3,5-Trinitrobenzene	1.36	0.861	
2,4-Dinitro-5-methylphenol	1.62	1.00	
1,3-Dinitrobenzene	1.62	1.00	
5-Methyl-2-nitrophenol	1.88	1.14	
3-Methyl-2-nitrophenol	1.88	1.14	
2,4-Dinitrotoluene	1.98 (2.28)†	1.19 (1.36)	
2,6-Dinitrotoluene	1.98 (2.28)	1.19 (1.36)	
3,5-Dinitrotoluene	1.98 (2.28)	1.19 (1.36)	
3,4-Dinitrotoluene	1.98 (2.28)	1.19 (1.36)	
2,3-Dinitrotoluene	1.98 (2.28)	1.19 (1.36)	
2,5-Dinitrotoluene	1.98 (2.28)	1.19 (1.36)	
2,4,6-Trinitrotoluene	2.03	1.22	
2,3,6-Trinitrotoluene	2.03	1.22	
2-Nitrotoluene	2.30	1.37	
4-Nitrotoluene	2.40	1.42	
Toluene	2.58	1.52	
1,5-Dimethyl-2,4-dinitrobenzene	2.95	1.72	52.50

*Log BCF = 0.542 log P + 0.124

†Calculated.

6 CONCLUSIONS AND RECOMMENDATIONS

The results of this study indicate that discharges from Composition B lines at LAP facilities contain, on an average, TNT and RDX at a ratio of 1.6/1 in the absence of pollution abatement treatment. SRI recommends that further toxicological investigations be performed using this component ratio because it represents a worst-case condition for which environmental impact data should be known.

The effects of sunlight photolysis on TNT/RDX mixtures can be studied in the laboratory with mercury lamps with Pyrex filters as an artificial light source. The preparation of photolyzed residues for toxicological evaluation can be achieved in the laboratory for acute and subacute investigations, but time and cost constraints would make the preparative method ineffective for long-term chronic studies.

In the condensate wastewater discharge at VAAP, 33 components were identified. The ratio of discharged components was found to be highly variable over the 12-month sampling period. A representative discharge was established by computer analysis. Toxicological and environmental impact data are limited for this array of compounds. SRI recommends that the environmental persistence of these compounds be considered as one criterion in establishing priorities for further toxicological investigations.

Condensate components for toxicological evaluations can be obtained through commercial sources and/or the synthetic methods described in this report. SRI recommends that analytical characterizations be performed on all materials used in toxicological evaluations because these classes of compounds are highly subject to isomeric contamination.

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Appendix

GLASS CAPILLARY GAS CHROMATOGRAPHIC ANALYSIS OF CONDENSATE COMPONENTS

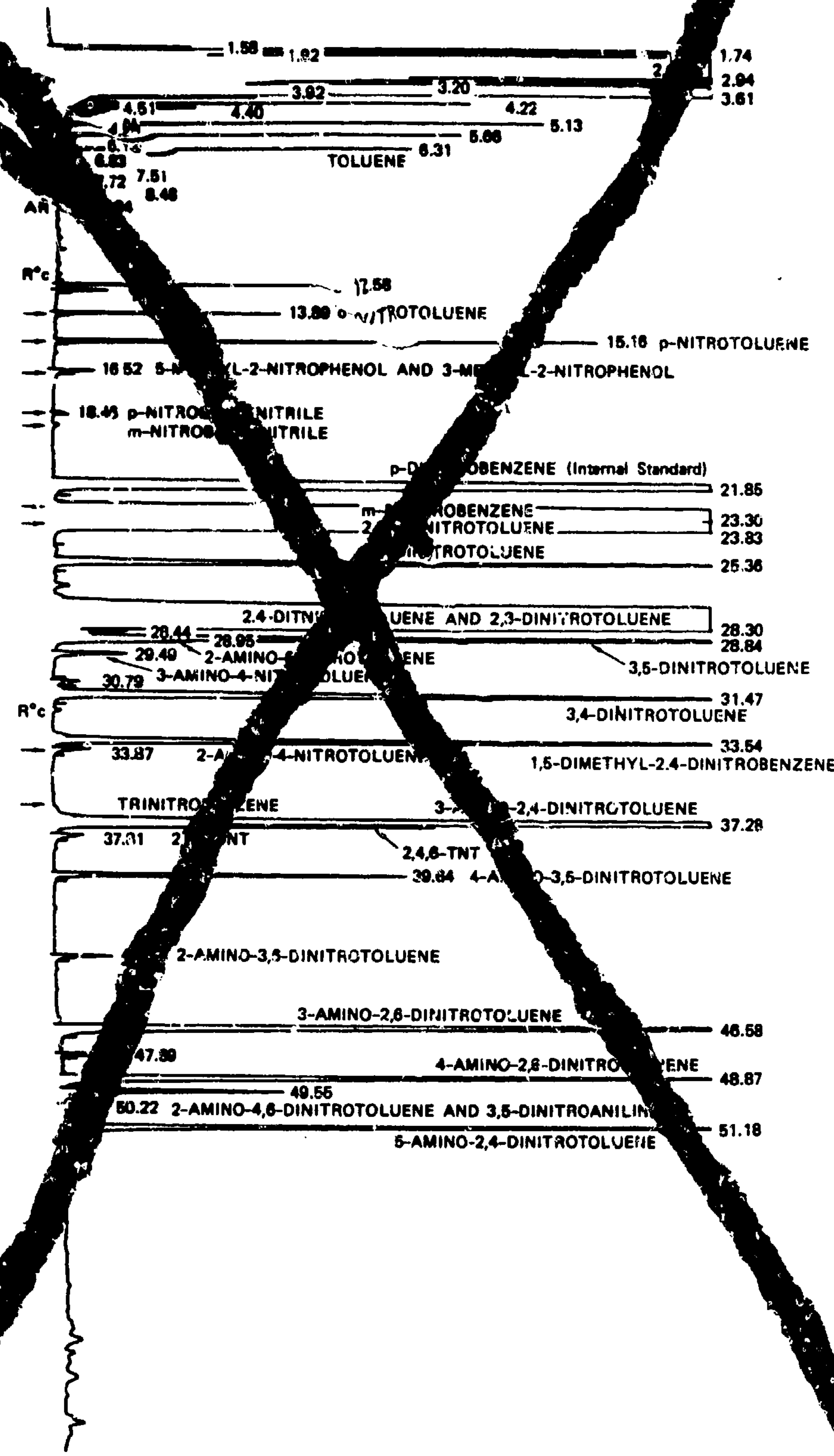
Because of the complexity of components discharged in VAAP condensate wastewater, a highly skilled mass spectrometrist is required to identify underlying components in major eluting chromatographic peaks. At times, this can only be achieved when the compounds being sought are known.

One way to alleviate this problem and to aid in qualitative and quantitative measurements is to increase the resolution capabilities of the chromatographic system. This can be achieved through the use of glass capillary columns.

Figure A-1 demonstrates the resolution capabilities that this system possesses on a synthetic mixture of the condensate blend. An actual VAAP wastewater extract appears in Figure A-2. In Figure A-2, 3-nitrotoluene is resolved from the 2- and 4-isomers and many more components appear that have not been identified. The majority of these new components are present in the parts-per-billion (ppb) range and represent a very small part of the total mixture.

The conditions under which these chromatograms were obtained are as follows:

- Instrument: Varian Model 2740 Gas Chromatograph modified for capillary gc.
- Column: 60 meter SE-30 glass column (J & W Scientific).
- Temperature: 140 (50 min hold) → 220 at 40 min (30-min hold).
- Split ratio: 190/1.
- Flow rate: 0.58 ml/min N_2.
- Detection: Flame ionization.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3.92
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4.40
4.22
5.13
5.66
TOLUENE 6.31
7.51
8.46
AR
R°c
13.89
15.16 p-NITROTOLUENE
16.52
18.45
(Internal Standard)
21.85
23.30
23.83
25.36
28.44
28.95
28.30
28.84
3,5-DINITROTOLUENE
29.49
30.79
R°c
31.47
3,4-DINITROTOLUENE
33.87
33.54
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2,4,6-TNT
39.84
2-AMINO-3,5-DINITROTOLUENE
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46.58
47.89
48.87
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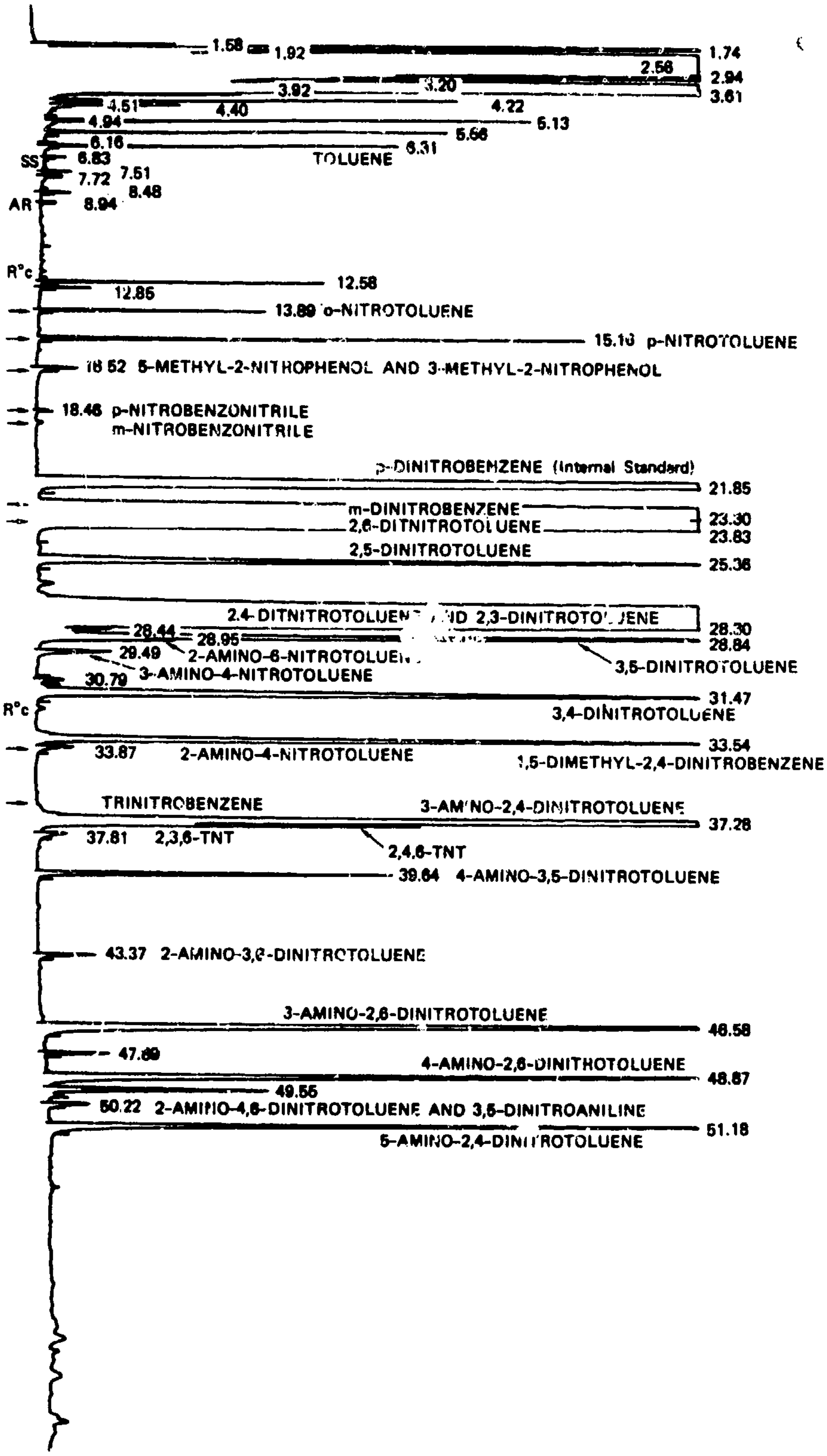
5-AMINO-2,4-DINITROTOLUENE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TOLUENE
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AR
8.94
R°c
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12.86
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15.10 p-NITROTOLUENE
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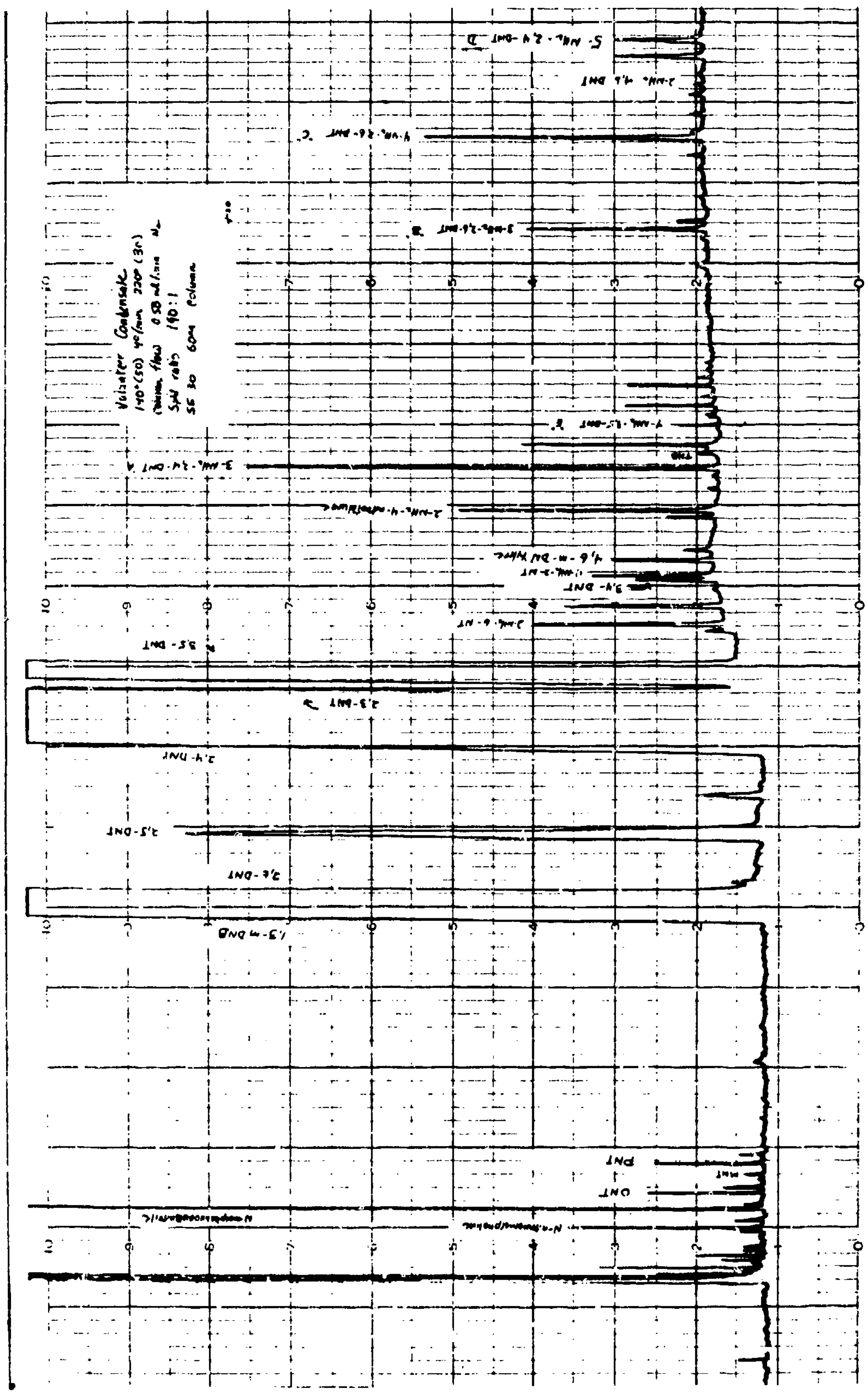

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